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Measurements of Formaldehyde and Hydrogen Peroxide in the California South Coast Air Basin

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Claremont, CA

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MEASUREMENTS OF FORMALDEHYDE AND HYDROGEN PEROXIDE IN THE CALIFORNIA SOUTH COAST AIR BASIN

by

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16. ABSTRACT

A chemiluminescent analytical technique for determining ambient air concentrations of formaldehyde (HCHO) was developed. The technique makes use of the chemiluminescent reaction between HCHO and gallic acid in the presence of hydrogen peroxide in a basic solution. Using this technique, HCHO concentrations were measured in the California South Coast Air Basin. Hydrogen peroxide (H_2O_2) and several other pollutants were also measured. Results showed that during moderate photochemical smog with ozone concentrations of 200 ppbv or less, typical HCHO concentrations of 5-15 ppbv were measured. Under conditions of intense photochemical smog, concentrations of HCHO were elevated to near 40 ppbv. At a coastal site, strong diurnal patterns for HCHO concentrations were measured. Measurements of HCHO and H_2O_2 were carried out in rain samples during the winter storm season of 1979-80. Typical patterns of HCHO concentrations showed a strong washout behavior with initial concentrations of 700-800 ppbm that decreased rapidly as the storm progressed. Hydrogen peroxide concentrations varied from a few ppbm to over 800 ppbm during the storm.

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ABSTRACT

This report describes work on the development of a chemiluminescent analytical system for the determination of formaldehyde (HCHO) in ambient systems, and the measurements of formaldehyde, hydrogen peroxide and other selected pollutants in the California South Coast Air Basin.

The chemiluminescent reaction between (HCHO) and gallic acid has been adapted for the determination of HCHO in ambient systems. The reaction takes place in the presence of a base and hydrogen peroxide. For the determination of ambient HCHO a trapping system is used consisting of a Saltzman bubbler with distilled water as the trapping reagent. The sample of HCHO collected in solution is analyzed directly using the chemiluminescent system. The system has a detection limit of 1 ppbv based on a one hour integrated sample. The chemiluminescent analytical technique has been tested with a wide variety of interfering substances commonly found in ambient samples. No significant interferences were found. Testing of this technique in parallel with other HCHO analytical techniques has shown that an unknown negative interference is present when sampling gas-phase HCHO under severe smog conditions. The chemiluminescent HCHO analytical instrumentation has been set up in an automated system which allows continuous analysis of HCHO in ambient air without operator attention.

Measurements of HCHO and hydrogen peroxide (H_2O_2) have been made in rain samples during the winter storm season 1979-80. Typical patterns for HCHO levels show a strong washout behavior with the initial levels approximately 700-800 parts per billion by mass (ppbm) and decreasing rapidly as the storm progresses. Hydrogen peroxide levels show a wide variation during the course of the storm. Levels ranged from a few ppbm to over 800 ppbm.

Measurements of HCHO have been made at several locations in the California South Coast Air Basin. When moderate photochemical smog is present, with ozone approximately 200 ppbv or less, primary sources appear to dominate the HCHO levels, and concentrations between 5-15 ppbv are typically measured. Under conditions of more intense photochemical smog HCHO levels near 40 ppbv have been measured. In measurements made at a coastal site in the basin, a strong diurnal pattern was observed in HCHO levels. The onshore flow of air contained HCHO at levels of around 5 ppb. The evening drainage winds bring large quantities of polluted air across the coast, and HCHO levels rise dramatically to around 30 ppbv. This HCHO is transported back into the basin and can serve as a photoinitiator for smog production.

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SECTION 1

INTRODUCTION

Control strategies for the reduction of secondary atmospheric pollutants are based primarily on kinetic computer models. These models developed from the interpretation of smog chamber studies and are verified by comparisons with ambient air measurements. The basic inputs for these models are data on levels of routine pollutants such as ozone (O_3), nitrogen oxides (NO_x), and hydrocarbons. Equally important to the model verification process are data on pollutants that exist in low concentrations, such as nitric acid (HNO_3), formic acid (HCOOH), formaldehyde (HCHO), and hydrogen peroxide (H_2O_2). Until recently, only limited data on the concentrations of these species were available (1).

The development of several new analytical techniques for analysis of ambient air has substantially enlarged the data base of measurements in trace species. These measurement techniques include:

- Long-path infrared spectroscopy (LPIR) capable of measuring HNO_3, HCOOH, and HCHO (2, 3)
- High-performance liquid chromatography (HPLC) dedicated to the measurement of HCHO and a broad spectrum of higher carbonyl species (4)
- Chemiluminescent H_2O_2 analytical technique that can be used for the measurement of H_2O_2 in air and rainwater (5).

In this report the development of a chemiluminescent technique for HCHO analysis is presented along with detailed measurements of HCHO and H_2O_2 in ambient air and rainwater.

Measurements of HCHO and H_2O_2 in ambient air and in rainwater are crucial to an understanding of atmospheric chemistry for several reasons:

- HCHO is easily photolyzed to form free radicals (6). If large quantities of HCHO are present in the early morning, photolysis of HCHO will accelerate photochemical smog formation.
- HCHO is a strong eye irritant (7). Reported eye irritation has decreased in the California South Coast Air Basin, and it is necessary to follow HCHO levels to determine if this reduction can be traced to HCHO or another species.
- Sinks for HCHO are very poorly defined. It is a highly water-soluble gas and would be expected to be removed rapidly by rain. Measurements of HCHO in rain can provide an estimate of the gas mixing ratio and removal efficiency of the rain-out process.
- H_2O_2 can serve as both a source and sink of free radicals. It is produced by the combination of two hydroperoxyl radicals (HO_2) photolyzed to form hydroxyl radicals (OH). Measurements of H_2O_2 can provide an insight into the concentrations of these radical species.
- Penkett et al, (8) and Martin and Damschen (9) have shown that H_2O_2 is probably the most effective oxidant for the heterogeneous conversion of SO_2 to sulfate. With the increasing SO_2 emissions in the Los Angeles area and the concern over acid rain it is important to quantitate H_2O_2 levels in rainwater.

Until recently ambient analyses of HCHO have been conducted using colorimetric techniques. These are limited in sensitivity and require

large amounts of technician time. Three new techniques for aldehyde analysis have been developed in the last few years, which will greatly add to the ease of HCHO data collection. The first new technique developed was based on the interpretation of infrared spectra taken with a long-path spectrometer (2). This technique has the advantage of providing unambiguous identification of HCHO, but samples cannot be preconcentrated and the detection limit is somewhat restrictive at 6 ppb HCHO. The two other HCHO analytical techniques use a preconcentration step that helps to increase the detection limit. One technique relies on the collection of aldehydes in a solution containing a derivatizing agent (4). Using high-performance liquid chromatography (HPLC), the derivatives are separated and quantitated. This technique has the advantage that a number of aldehyde species can be quantitated. The other technique is described in detail in this report, and uses the chemiluminescent reaction between HCHO and gallic acid to quantitate HCHO concentrations. This technique has sufficient sensitivity for ambient determinations of HCHO and is automated for continuous operation.

A series of ambient HCHO measurements has been made in Los Angeles since 1960 (3, 10, 11, 12,). These measurements compose a limited data set which give an indication that a downward trend in HCHO levels may be present. In the first set of measurements during 1960-61, HCHO levels averaged 45 ppb in downtown Los Angeles, and levels above 70 ppb were not uncommon (10, 11). In 1968 measurements of HCHO at locations about 20 miles east of Los Angeles, Scott Research Laboratories found levels up to 120 ppb (12). The levels of HCHO measured at the downtown locations would be expected to be mostly primary HCHO, while measurements made in the eastern part of the basin will represent primary plus secondary HCHO.

The most recent set of HCHO measurements has been made at locations in Claremont and Riverside, California. These locations are at the eastern edge of the California South Coast Air Basin, where photochemically produced ozone reaches a maximum. Measurements of HCHO using LPIR indicate average levels of HCHO to be 20-40 ppb under conditions of moderate photochemical smog, and a maximum HCHO level of 71 ppb was measured under severe smog conditions (O_3 = 454 ppb) (3). Looking at these three sets of HCHO measurements as a group it suggests that HCHO levels have decreased substantially in the Los Angeles Basin. This potential decrease in HCHO levels would tend to correlate with the reduction in non-methane hydrocarbon (NMHC) levels observed in the California South Coast Air Basin. From 1964 to 1974 the NMHC levels have decreased by about 20% average over the entire California South Coast Air Basin. This reduction is due in large part to the implementation of catalytic coverters on automobiles. The use of catalytic converters also brings about a reduction in HCHO emissions. Automobiles with catalytic converters emit HCHO at about 15-40 mg/mile. Without control devices HCHO emissions are in the range of 45-200 mg/mile (14, 15).

This decrease in HCHO levels is beneficial in that it reduces the photochemical reactivity of the air mass and also the eye irritation produced from HCHO. Continual monitoring of HCHO in the Los Angeles Basin is necessary for two reasons. (1) The continued increase in miles traveled by diesel vehicles could substantially increase the primary HCHO emissions in the basin. (2) The apparent reactivity of the Los Angeles air mass has been changing in the past few years as the ozone maximum moves closer to the emission sources in the central Los Angeles

area. This reactivity change may be due in part to changes in HCHO levels, and a detailed program of measurements is necessary to ascertain this.

Only two studies of H_2O_2 levels in the California South Coast Air Basin have been published. In the first study Bufalini, Gay, and Brubaker found H_2O_2 levels up to 180 ppb (17). Kok et al. measured H_2O_2 levels of 30-40 ppb during July and August, 1977 (18). These studies were of such a limited nature that it is impossible to suggest that any trends are apparent. The development of the chemiluminescent technique for measurement of H_2O_2 (5) has provided a rapid and sensitive method for H_2O_2 determinations and made it possible for extended studies to be conducted.

The only known source of H_2O_2 in ambient air is through photochemical production. Detailed measurements of H_2O_2, including diurnal variations, will be useful in elucidating the reaction pathways for H_2O_2.

Measurements of HCHO in rainwater have previously been reported for nonurban locations (19, 20, 21). These studies show that HCHO is rapidly rained out, and concentrations of HCHO ranged from 6 ppbm for remote areas (21) to a high of 220 ppbm for a coastal area in Massachusetts (19). The work reported here is unique in that these are the first known measurements of HCHO in rainwater for an urban area. The high levels of gas-phase HCHO encountered in the California South Coast Air Basin coupled with well-defined frontal precipitation events provide an excellent format for detailed studies on the removal processes of HCHO in rainwater.

Only three previous studies on concentrations of H_2O_2 in rain are known to have been previously published (22, 23, 24). These studies were performed at widely separated locations and show H_2O_2 concentrations to be in the typical range of 100-200 ppbm with differences depending on the nature of the storm. Since H_2O_2 is important in oxidizing SO_2 (8, 9), it is necessary to obtain a more detailed understanding of H_2O_2 in rainwater to assess the potential for SO_2 conversion.

To bridge some of these gaps in the knowledge of atmospheric HCHO and H_2O_2, a three-year program was initiated in 1979. The objectives of this program were threefold:

1. Develop and test a chemluminescent instrument for the determination of HCHO in ambient air and rainwater.
2. Conduct measurements of HCHO and H_2O_2 in rainwater.
3. Conduct measurements of HCHO, H_2O_2, and other species at various locations in the California South Coast Air Basin

SECTION II

CONCLUSIONS

The chemiluminescent reaction between gallic acid and formaldehyde (HCHO) has been developed into a technique to quantitate HCHO in aqueous solution. The detection limit for HCHO is better than five parts per billion by mass (ppbm) for a one milliliter sample. Laboratory and field studies using the technique for the determination of HCHO in rain water indicate that the technique is relatively free from interferences. Measurements of gas-phase HCHO in ambient air indicate that a negative interference is present under heavily polluted conditions. The nature of the interference is not known.

Measurements of hydrogen peroxide (H_2O_2) and HCHO were made on seven precipitation events during the winter months of 1980 and 1981. Formaldehyde levels in the initial precipitation are generally 500-700 parts per billion by mass (ppbm) and decrease rapidly to approximately 100 ppbm. These data indicate that a significant portion of the HCHO present in rainwater is incorporated into the drops below cloud level. Hydrogen peroxide measurements were also made on the same precipitation samples. In contrast to the HCHO levels, H_2O_2 levels varied considerably during the course of a precipitation event with no discernable patterns. This data suggests that significant amounts of H_2O_2 are generated in situ in cloud and rain droplets and that gas-phase H_2O_2 contributes little to the precipitation concentrations.

Gas-phase measurements of HCHO and H_2O_2 have been made at several locations in the California South Coast Air Basin during the summer months of 1979 and 1980. The measurements concentrated on examining the

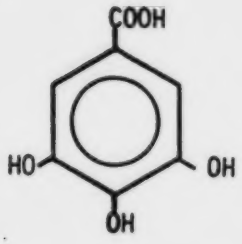
spatial and diurnal variations in HCHO and H_2O_2 levels. Background levels of HCHO range from 5-10 parts per billion by volume (ppbv) and reflect levels from primary sources. Photochemically produced HCHO gave levels ranging from 10-50 ppbv with the HCHO level correlating well with the level of photochemical ozone.

The quality of the gas-phase H_2O_2 data is in question because of a variable ozone interference that can produce either a positive or negative interference. Hydrogen peroxide measurements made in the absence of ozone, generally at night, show relatively constant levels from 2-5 ppbv. Measurements of gas-phase H_2O_2 made in the present of photochemical smog are widely varying, ranging from 2-12 ppbv, with no apparent correlation with smog intensity.

SECTION III

CHEMILUMINESCENT FORMALDEHYDE ANALYTICAL TECHNIQUE

The chemiluminescent reaction of 3, 4, 5 trihydroxy benzoic acid (gallic acid) with HCHO was first discovered by Trautz and Schorigin in 1905 (25). Equation 1 gives the general reaction chemistry:



$$+ \text{HCHO} \rightarrow h\nu + \text{products} \qquad (1)$$

The products from the reaction have not been completely characterized, but appear to be polymeric breakdown species from the gallic acid. The chemiluminescence arises from singlet oxygen emission. The major emission bands are at 643, 702, and 762 nm. The efficiency of singlet oxygen production is less than one-percent based on HCHO as the limiting reagent. This low singlet oxygen production coupled with the reduced sensitivity of photomultiplier tubes (PMT) in the red region of the spectra have previously limited the analytical applications of this reaction since poor detection limits were obtained. A recent study on the chemistry of this reaction has provided a better understanding of the changes needed to improve the singlet oxygen production (26). In addition advancements in PMT technology have improved red response considerably, effectively increasing the detection of the chemiluminescence from this reaction.

The first analytical application of this reaction was by Slawinska and Slawinski (26). These workers used a wet chemical flow system to determine HCHO in natural waters. The system showed no significant interferences in the analysis for HCHO, and a detection limit of 3 ppbm for HCHO was obtained.

To adapt this analytical technique for ambient air monitoring of HCHO several modifications needed to be made to the original system as designed by Slawinska and Slwainski (26). These include:

- Modification of the reagent system so that the system could operate for 24 hours with no major change in sensitivity
- Testing of the analytical system for interferences commonly encountered in ambient air
- Design of an automated flow system suitable for continuous monitoring of HCHO without the need for operator attention.

A. Design of the Analytical Flow System

The flow system for the chemiluminescence (CL) HCHO analytical technique was designed to follow the general format of the CL H_2O_2 system (5). Figure 1 gives the schematic diagram of the CL HCHO analytical system set up for manual analysis of liquid-phase HCHO samples.

The analytical system is configured using the following components:

Photomultiplier tube (PMT): Hamamatsu R928P

PMT housing: Products for Research TE-202

Electrometer: Keithley 416

Noise filter: Frequency Devices 740 LT-1

Mass Flow Controller: Tylan FC-260, range 0-50 sccm

High voltage power supply: Bertan Associates PMT-20 AN option 1

Peristaltic pump: Technicon Auto Analyzer Pump I

The PMT and housing were chosen to provide good capabilities for detection of red light and a short pathlength for the light.

In the absence of chemiluminescence the PMT signal originates from the thermal emission of electrons in the dynode chain. This is called dark current. The electrometer will amplify all signals with frequency

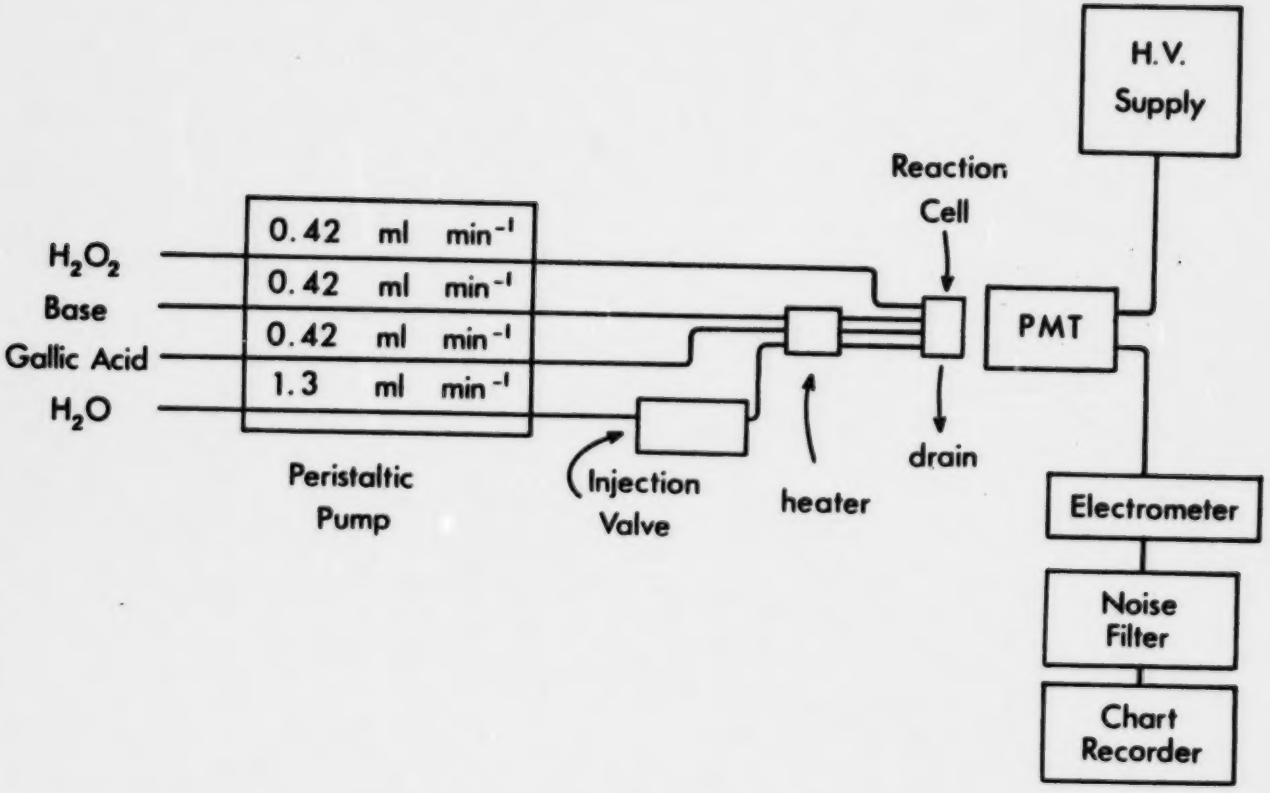


Figure 1. Flow system diagram for the chemiluminescent HCHO analytical instrumentation

of less than 5 hertz and this includes a substantial portion of the dark current. The frequency of the chemiluminescent signal is about 0.1 hertz and a substantial improvement in detection limit can be obtained by adding a low pass filter between the electrometer and the chart recorder. The filter is set up to pass all signals below 0.5 hertz. eliminating a major portion of the noise in the dark current. With the reduction in dark current noise the detection limit is increased from 30 ppbm to 5 ppbm HCHO.

The reagent flow rates were chosen arbitrarily and the reagent concentrations optimized on the basis of these flows. The system was set up to pump each of the reagents individually into the cell, since they decompose in a period of hours if pre-mixed. To insure mixing in the cell a stream of gas is introduced. The flow of this gas stream must be well regulated to maintain constant mixing and reproducibility in the analytical system. The use of a mass flow controller is highly recommended.

The reaction cell has been designed to allow the gas stream to bubble up through the cell, mixing the reagents and carrying the reaction products out of the cell. Figure 2 shows a full-size drawing of the cell. The light from the chemiluminescent reaction is very diffuse, and the placement of a mirror behind the cell does not appreciably increase the signal as measured by the PMT.

The reagent concentrations were optimized using a Simplex Search technique (27, 28). The optimized concentrations chosen were:

gallic acid = 9.2×10^{-3} M

hydrogen peroxide = 9.1×10^{-2} M

NaOH = pH 12.2

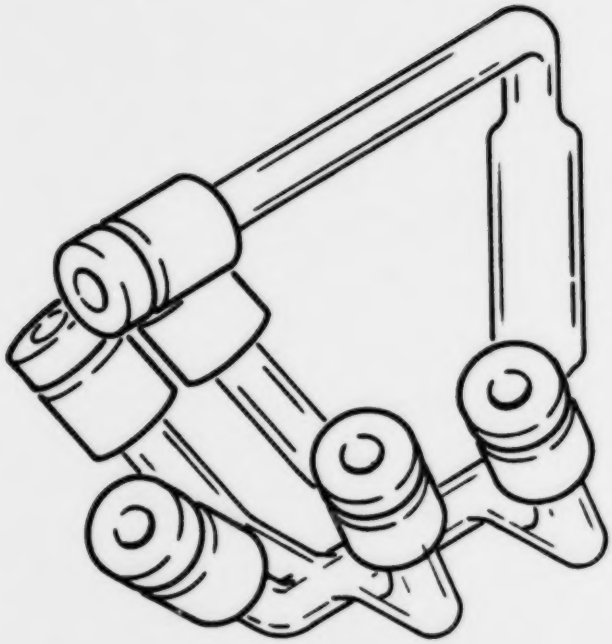


Figure 2. Drawing of the reaction cell for the chemiluminescent HCHO analytical instrumentation. The cell is shown full size. The stirring gas is added at the port to lower left, with the reagents added on the side arms.

The system response is not highly sensitive to the concentrations of gallic acid or H_2O_2. The NaOH concentration is critical, and slight deviations from pH 12.2 can cause a sharp decrease in signal. Figure 3 shows the response of the system with changes in pH.

The type of gas used also influences the sensitivity. The use of air in place of nitrogen increases the signal by a factor of 1.8 and the use of oxygen increases sensitivity by a factor of 2.1 over nitrogen. For the work discussed in this report, air was the mixing gas. The equilibration of the mixing gas with the reagents is sufficiently fast that it is not necessary to pre-equilibrate the standards or samples with the mixing gas.

Over the temperature range 293-313°K the chemiluminescence output decreases as a linear function of the inverse temperature (26). The change in output is about -50% for a temperature increase of 10°K over the range 293-313°K. Below 293°K the chemiluminescence output drops off due to kinetic considerations. The measurements detailed here were all conducted under temperature controlled conditions with a temperature range of 293-298°K.

Reagent-grade chemicals are suitable for the analytical system. The H_2O_2 is made up by dilution of 30% material. Some bottles have been found to contain high levels of HCHO causing an elevated baseline leading to a reduction in sensitivity. The background signal is typically only 5-10% above the dark current and any elevation above this may indicate reagents contaminated with HCHO. High-quality distilled water or water from a cartridge purification system using both charcaol and ion-exchange cartridges is suggested. Commercially available HPLC water should be avoided as these contain variable amounts of HCHO. This water is irradiated

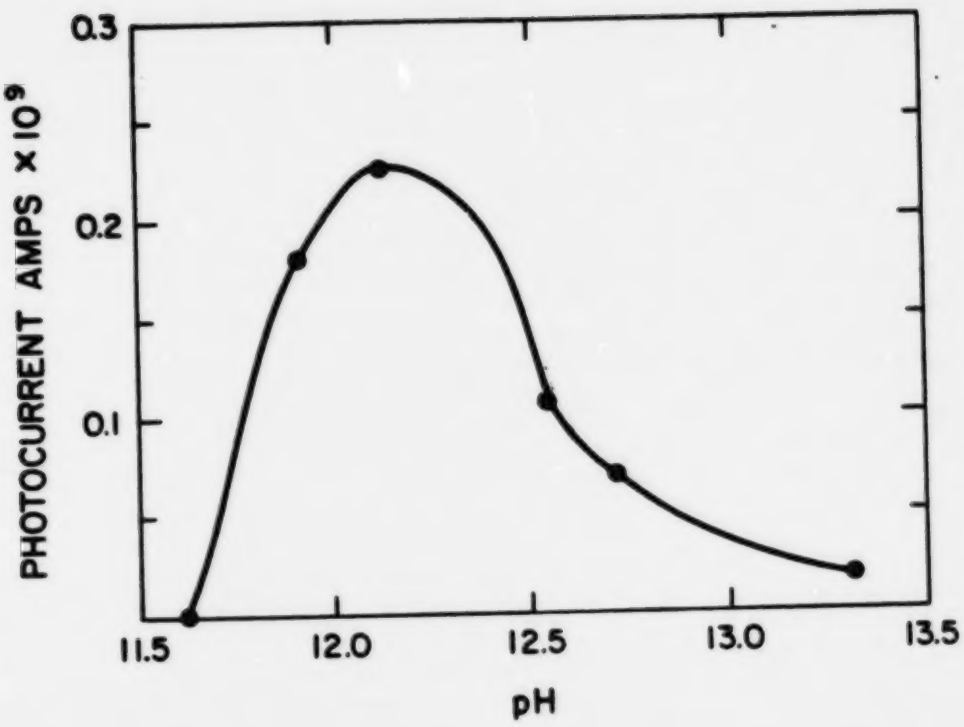


Figure 3. Changes in sensitivity for the chemiluminescent HCHO analytical system as a function of reagent pH.

with UV to remove organics, and this treatment appears to degrade some of them to HCHO.

Aqueous-phase HCHO standards are best prepared by dissolving sodium formaldehyde bisulfite in water. This provides a convenient gravimetric standard. Commercial formalin solutions (37%) contain large quantities of methanol and other species that make them undesirable as standard materials.

The analytical instrumentation is capable of handling approximately 10-15 HCHO samples and standards per hour. The analytical procedure involves preparation of the reagents and allowing them to run through the system for about five minutes to establish a baseline. The electronics can remain on continuously so that no warm-up time is involved for them. Following the establishment of a baseline a series of standards should be analyzed to set up the calibration curve. Very little drift is encountered during the course of an analytical sequence and only periodic span checks are required after the initial calibration. Analysis of samples can proceed as rapidly as the chart recorder trace returns to the baseline.

Figure 4 shows the response of the analytical instrumentation to injections of 100 ppbm HCHO standard. The detection limit of the instrumentation is approximately 5 ppbm HCHO. The present limiting factor is the dark-current noise Recent development of a microprocessor signal averaging system for chemiluminescent techniques (29) could potentially lower the detection limit. The system has been tested for linearity up to 1,000 ppbm HCHO, and the correlation coefficient for the concentration range 10-1000 ppbm is 0.995.

For measurement of gas-phase HCHO levels the samples are collected in aqueous solution using Saltzman-type bubblers modified with extra

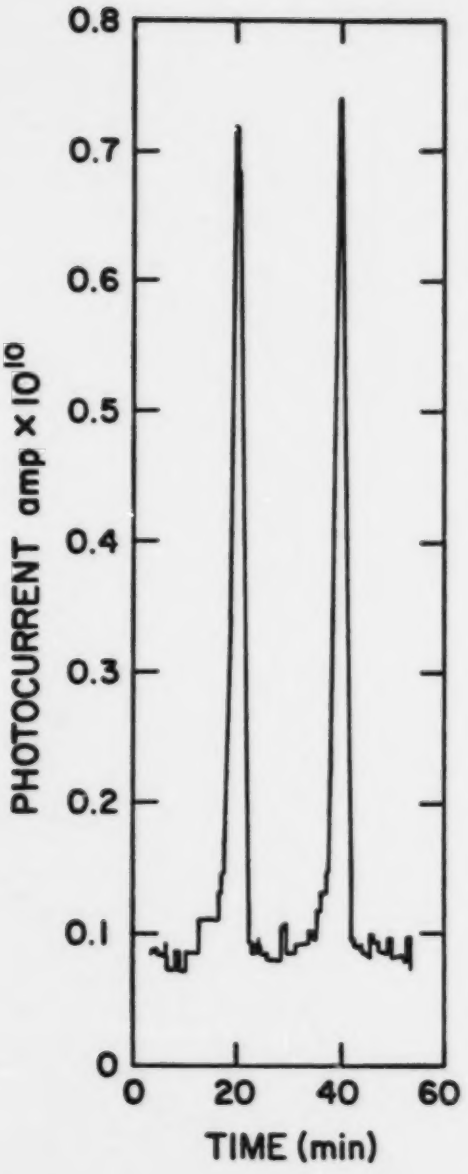


Figure 4. Response of the chemiluminescent HCHO analytical instrument to standards of 100 ppbm HCHO.

coarse frits. The collection efficiency of these bubblers for HCHO has been found by Altshuller et al. to be 84% (11). A series of tests were run in our laboratory using multiple bubblers in series to check this collection efficiency. Over a wide range of samples with HCHO concentrations ranging from 10-200 parts per billion by volume, an average of 83 ± 5% was obtained for the collection efficiency using an aqueous trapping solution in a single bubbler. These samples were derived from laboratory mixtures with a relative humidity of less than one percent to ambient air with varying humidity. No specific checks for collection efficiency as a function of humidity were done. A sample flow rate of 1 standard liter-per minute is used. For a sample collection time of one hour the detection limit for gas-phase HCHO is 0.5 ppbv.

B. Interference Studies

An extensive series of interference tests has been run on the chemiluminescent (CL) HCHO analytical system. These have included single component laboratory studies, smog chamber studies, and extensive ambient air intercomparison studies. Interferences would be expected to arise from two sources, a negative interference from species that will quench the singlet oxygen emission and positive interferences for species which will break down the gallic acid and produce singlet oxygen.

Table 1 gives the results of the laboratory tests involving a wide variety of species that could act as potential interferents in the system. No significant interferences are found from any of the tested species. Slight positive interferences are noted from glyoxal and hydroquinone. The ambient concentrations of these are unknown, but presumably they would be present in such low quantities that no interference would be noted.

Table 1

Effect of Interfering Compound
on the Chemiluminescent Formaldehyde
Analytical System

Compound	Concentration[1]	% Interference[2]
Acetaldehyde	1 ppmm	0
Acetic Acid	1 ppmm	0
Benzene	1 ppmm	0
Formic Acid	1 ppmm	0
Glyoxal	1 ppmm	5%
Hexane	1 ppmm	0
Hydroquinone	1 ppmm	3%
Methyl Alcohol	1 ppmm	0
Methylethyl Ketone	1 ppmm	0
Methyl Nitrate	1 ppmm	0
Nitric Acid	1 ppmm	0
Nitric Oxide	1 ppmv[3]	0
Nitrogen Dioxide	1 ppmv	0
Ozone	500 ppbv	0
Peroxyacetic Acid	1 ppmm	0
Sulfuric Acid	1 ppmm	0
1-Pentene	1 ppmm	0
Cu (II)	100 ppbm	0
Mn (II)	100 ppbm	0
Fe (III)	100 ppbm	0

[1]All interference tests were done with and without HCHO present. When present the HCHO concentration was 50 ppbm.

[2]The percent interference is the percentage of the species tested that will appear as HCHO.

[3]The gas-phase species were examined by bubbling them through 50-ppbm HCHO for 30 minutes under conditions similar to ambient air sampling.

A limited series of smog chamber studies was conducted in conjunction with the chamber facility at EPA-RTP (30, 31). In this study the HCHO levels were measured by both an LPIR system and the CL technique. For a series of nine HCHO samples involving five standard samples and four mixtures of aldehydes the following regression equation was obtained:

$$HCHO(CL) = 1.92\ HCHO(LPIR) - 32,\ R = 0.90 \quad n = 9$$

The units for the regression equation are in parts per billion by volume of HCHO. The samples covered the HCHO concentration range 10-67 ppbv as measured by LPIR. A good correlation coefficient is obtained, but a relatively high slope is observed. This suggests a calibration offset in one of the techniques. A series of five chamber runs was also conducted. These runs consisted of approximately 5 ppmv of olefins irradiated in the presence of O_3 or HONO as the radical source. The regression equation for this limited data set is:

$$HCHO(CL) = 1.61\ HCHO(LPIR) + 60,\ R = 0.86 \quad n = 5$$

The HCHO concentration ranged from 30-277 ppb as measured by LPIR. In comparing this result to that obtained from the standard samples the results are generally consistent. The slightly lower slope for the irradiated samples suggests a negative interference, but the data set is too limited to draw any major conclusions.

A series of ambient air comparisons between the CL HCHO analytical technique and the LPIR and HPLC techniques has been conducted. Figure 5 shows two separate comparison studies between the LPIR and the CL HCHO analytical techniques. The data shown in Figure 5(a) are for August 31, 1979. The concentration of photochemical smog was relatively low (O_3 maximum, 192 ppbv), and the data show good agreement for HCHO measurements with the two techniques. In Figure 5(b) results of HCHO comparison

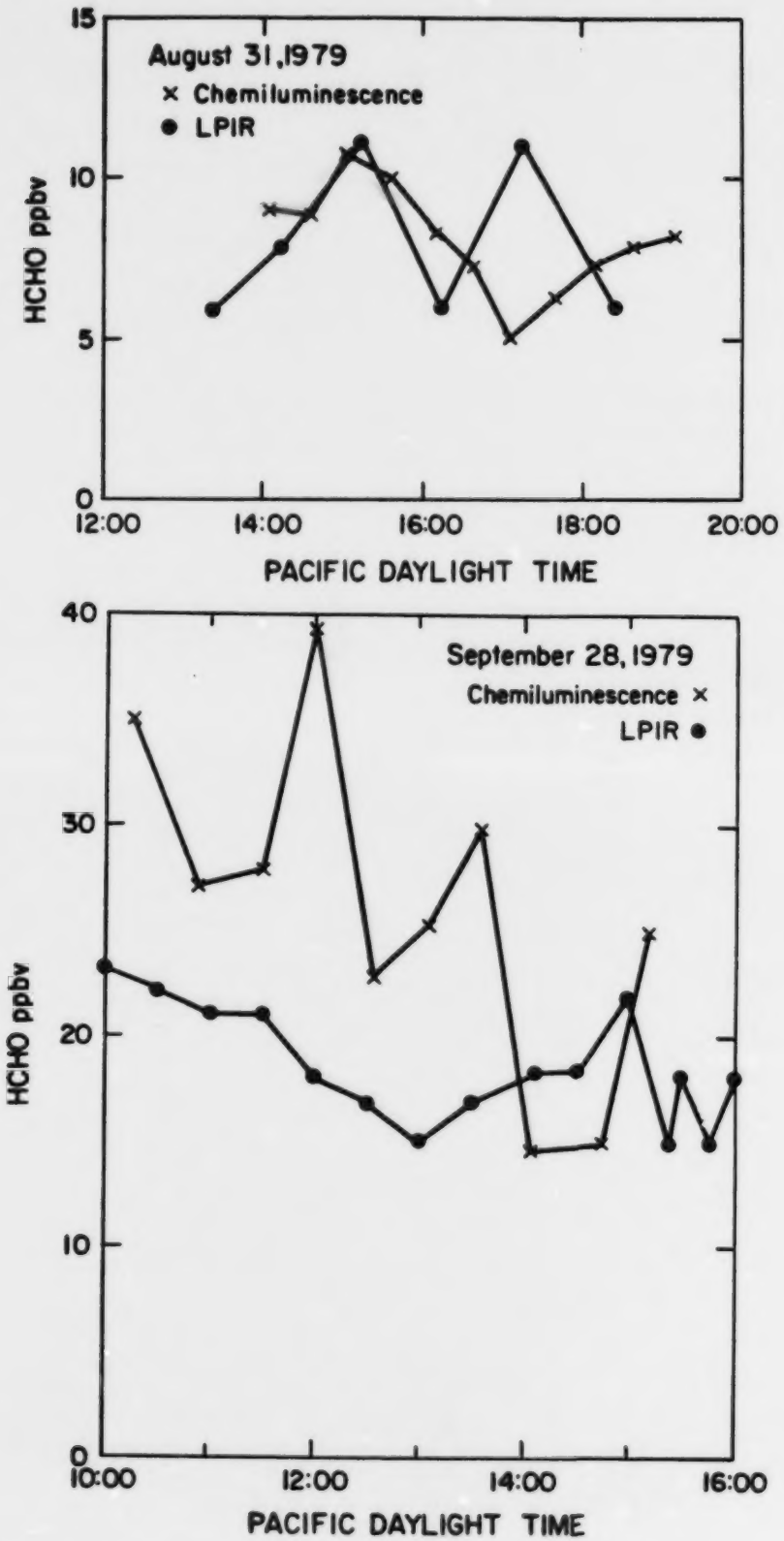


Figure 5. Comparison of ambient HCHO measurements by LPIR and chemiluminescence.

measurements on September 28, 1979, are shown. The maximum O_3 concentration was 150 ppb. These HCHO levels are relatively high considering the low amount of photochemical smog present. The data show a moderate amount of scatter, and the CL technique gave slightly higher HCHO levels.

A more extensive comparison study of HCHO analytical techniques was conducted during 1980 under the sponsorship of the Coordinating Research Council (32). This study involved the HPLC aldehyde analytical technique operated by Dr. Daniel Grosjean of Environmental Research and Technology of Westlake Village, California, and the chromotropic acid (CA) and CL HCHO analytical techniques operated by Harvey Mudd College personnel. This study involved three parts, including measurements of HCHO from standard samples and measurements under moderately polluted and heavily polluted ambient air conditions. In the first two phases of this study the general agreement between the analytical techniques was good for HCHO, and no systematic biases were noted in any of the data. The third phase of the study was conducted under conditions of intense photochemical smog (O_3 levels from 300-450 ppbv). The HPLC and CA techniques gave comparable results for HCHO, but the CL technique was low by an average factor of 3. The CL data show a distinct diurnal variation, indicating that the interference is proportional to the concentration of HCHO present.

The low results as obtained by the CL technique cannot be traced to a reduced collection efficiency since a single sample was collected for both the CA and CL techniques and then divided for analysis. Potentially the interference involves quenching of the singlet oxygen emission. The species responsible for this interference is unknown. Additional studies are planned to examine this problem.

The system has been tested extensively for response to interfering species. The majority of the studies have indicated relative freedom from interferences with the ambient air measurements made during the fall of 1980, indicating an unknown negative interference. This instrumentation is in the developmental stages and must be used with caution in analyzing any samples for HCHO because a complex matrix of potentially interfering species is certain to be present. At this time the most reliable technique to check for interferences would appear to be by standard addition. If a slope substantially different from the calibration curve or a nonlinear standard addition curve is obtained the sample should be examined further for interferences.

C. Automated HCHO Analytical System

To obtain sufficient data on ambient HCHO levels from modeling data bases or to assess exposure levels the utilization of a continuous HCHO sampler is necessary. Several continuous HCHO analyzers have been constructed but none have the sensitivity required for ambient monitoring (33, 34, 35). The CL HCHO analytical system is very suitable for continuous automated sampling of aldehydes since the basic analytical technique is based on a flow system and the reagents are sufficiently stable for the system to operate for 24 hours without operator intervention. The continuous HCHO analytical system collects the sample using a fritted bubbler for sample collection and automatically transfers the sample to the analytical system for quantitation.

Figure 6 gives the basic flow system for the automated HCHO analytical system. The unit is set up to collect and analyze ambient samples of HCHO as well as calibration standards following each ambient sample.

The instrument is based on a 60-minute cycle that includes one ambient analysis and two calibration standards.

The following sequence describes the instrument operation. Figure 6 details the location of the valves and pumps.

1. At the termination of an ambient sampling period (59 minutes) pump P_2 and valves V_2, V_3, and V_4 are activated. The sample is pumped from the impinger through the injection valve loop. After 8 ml have been pumped out, insuring flushing of the sample loop, the injection valve V_3 is deactivated and the ambient sample containing HCHO is injected into the analytical system. The remainder of the sample is pumped to waste.
2. The bubbler is filled for a rinse cycle by deactivating V_2 and V_4 and activating pump P_1 and valve V_2.
3. The bubbler is emptied of the rinse water by repeating step 1 with V_3 in the deactivated position, allowing the rinse to go through the bypass loop.
4. The bubbler is filled with 10 ml of water for sampling by repeating step 3.
5. Steps 1-4 require one minute of total time. Twenty minutes after the ambient sample is analyzed a calibration sample is injected by activating P_2 and V_3 and V_4. A second calibration sample is injected 40 minutes after the ambient sample.

A 60-minute cycle time was chosen since it provides both sufficient time resolution of ambient HCHO measurements and preconcentration of the sample. All of the valves and tubing in the flow system are constructed of Teflon to minimize contamination.

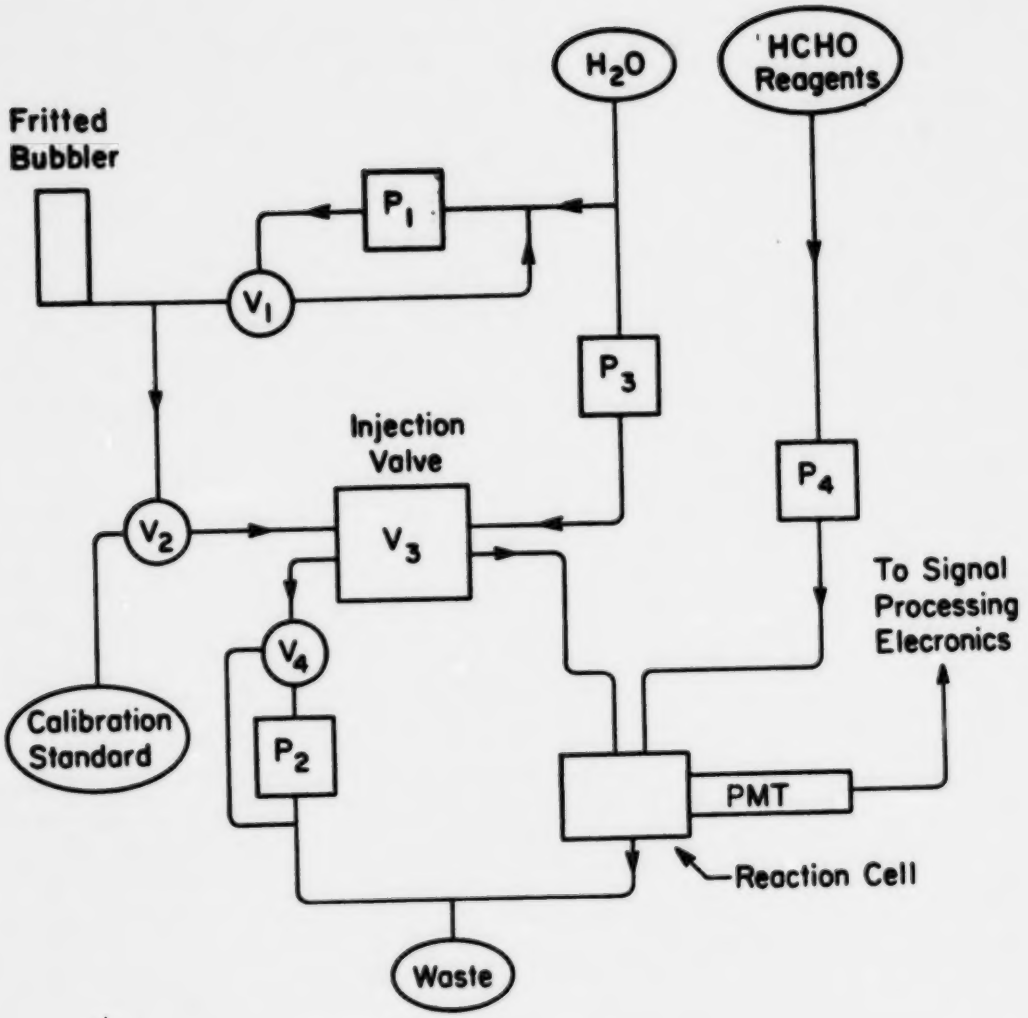


Figure 6. Flow system for the automated HCHO analytical instrumentation.

SECTION IV

MEASUREMENTS OF HCHO AND H_2O_2 in RAINWATER

Extensive measurements of HCHO, H_2O_2, and pH were made on seven precipitation events during the winter months of 1980 and 1981. The sampling was conducted from the Harvey Mudd College campus in Claremont, California. Samples were collected using a refrigerated fractionating collector that collected the precipitation in constant increments. These increments varied between 0.8 and 1.4 mm and were set for each precipitation event.

The precipitation in the California South Coast Air Basin typically arises from northern frontal storms which form out on the Pacific Ocean and move in a west-to-east pattern across the basin. This flow pattern makes the basin an ideal location to study H_2O_2 and HCHO in rain since the storms form in a region of relatively clean air and pick up contamination as they move east across the basin.

No previous studies of HCHO levels in rain in the Los Angeles area and only one limited study on H_2O_2 levels (22) have been published. A very detailed multilocation study on acidity in this region was conducted by Liljestrand from 1976-1979 (36). This was a detailed analysis of pH, ion compositions, and organic concentrations.

Appendix A gives the detailed analytical data for all of the sampled precipitation events. Three of these sets of data will be analyzed in detail in this report as they demonstrate the general behavior for HCHO and H_2O_2 in rainwater.

Table A-1 gives the detailed analytical data for pH, HCHO, and H_2O_2 collected January 27-29, 1980, in a southern tropical storm. Figure 7 details the HCHO and H_2O_2 levels for the first hours of this precipitation event. Figures 8 and 9 show HCHO and H_2O_2 data for precipitation events collected January 28-29 and February 8-9, 1981, respectively. The tabulated data for these storms are given in Tables A-4 and A-5.

The HCHO levels show a similar trend for most of the storms sampled. Initial levels are several hundred ppbm and decrease rapidly to a general level of about 50 ppbm. This behavior suggests that HCHO is being incorporated into the rain below cloud level and is washed out. The influence of continued precipitation on suppressing HCHO levels in rain is strongly demonstrated in Figure 6, the precipitation collected on January 27-29, 1980. The initial HCHO level was 670 ppbm and dropped to 60 ppbm in the course of 0.5 cm of precipitation. During the time period 10:05-10:43 an intense precipitation shower of 11 mm was collected. The average HCHO level was about 75 ppbm and did not go below 30 ppbm. This presumably is the residual HCHO incorporated at cloud level, since it is not washed out. Immediately following this intense shower the rain intensity decreased and after a 2-hour lapse in precipitation the concentration in subsequent rainwater had increased to 220 ppbm. The same type of strong washout dependence is seen in almost all of the HCHO data. In only one case, February 25-26, 1981, Table A-6, was the initial HCHO concentration below 100 ppbm. This precipitation event was characterized by very low concentrations of HCHO in all of the samples for some unknown reason.

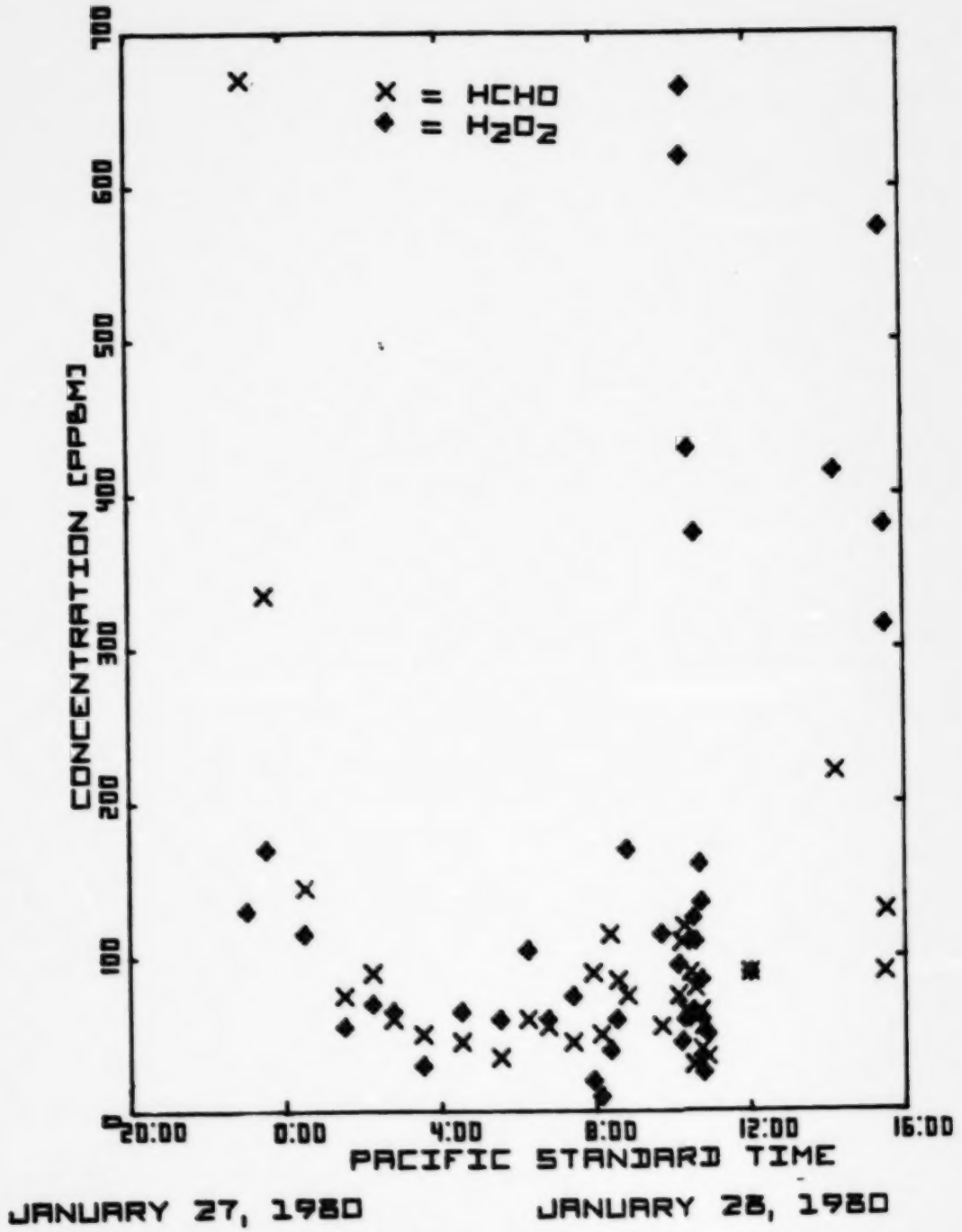


Figure 7. HCHO and H_2O_2 levels in rainwater collected January 27-28, 1980.

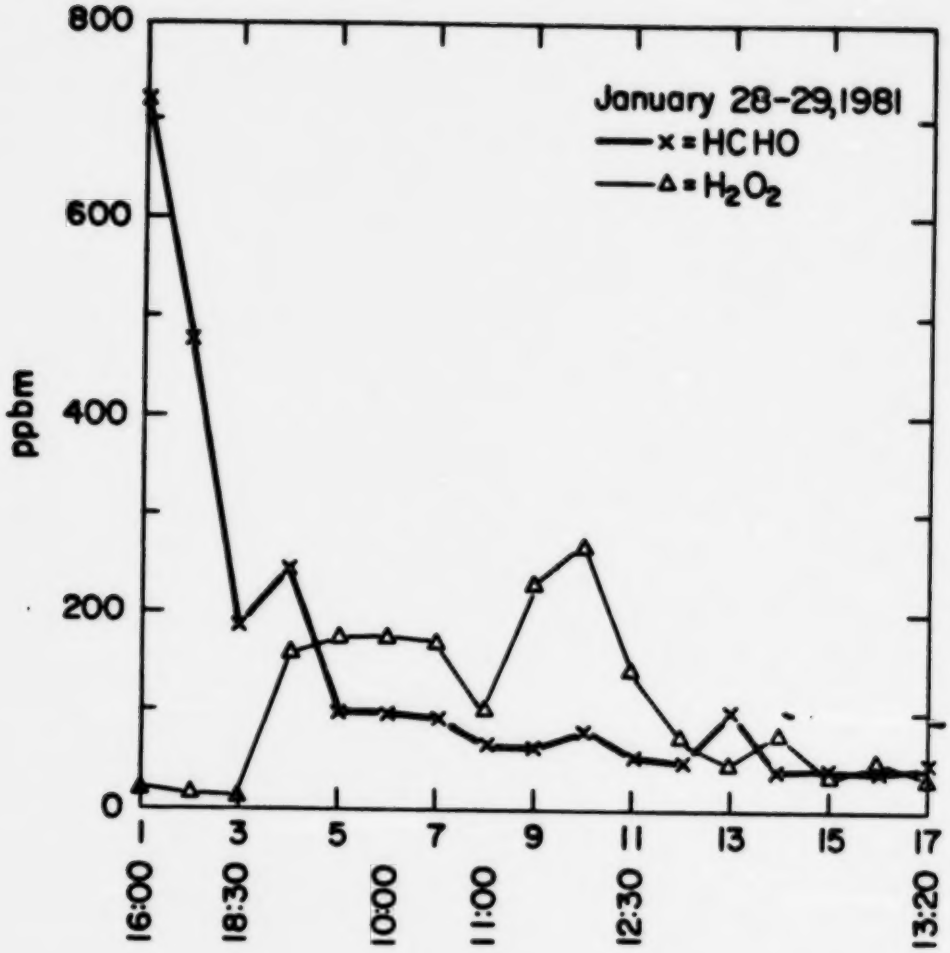


Figure 8. HCHO and H_2O_2 measurements in rainwater collected January 28-29, 1981.

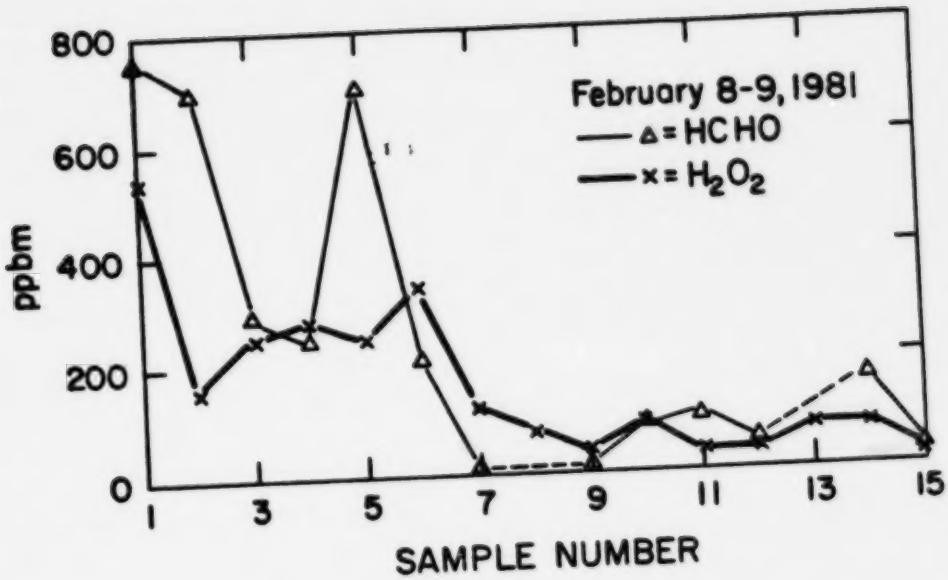


Figure 9. HCHO and H_2O_2 levels in rainwater collected February 8-9, 1981. The precipitation began 18:00 on February 8 and terminated 15:00 on February 9, 1981.

The H_2O_2 levels in rainwater do not show a pattern like that for HCHO. Hydrogen peroxide levels are extremely variable during the course of a storm. This diversity in H_2O_2 levels suggests that H_2O_2 is incorporated into the rain at the cloud level. In addition to gas-phase H_2O_2 as a source of H_2O_2 for rain, O_3 and H_2O can react to produce H_2O_2, according to recent studies (37, 38). This could be a variable source of H_2O_2 during the course of a storm.

In Figure 6 very little correlation is noted between H_2O_2 and HCHO levels. The highest H_2O_2 levels are observed during the period of most intense rainfall from 10:05-10:43. In this storm as in the other three where H_2O_2 was measured the H_2O_2 levels show no washout dependence. This suggests origins for H_2O_2 other than gas-phase H_2O_2, which would show a strong washout dependence. Detailed meteorological analysis on these storms will be necessary to completely understand the mechanism for the incorporation of H_2O_2 into rainwater.

No gas-phase mixing ratios for H_2O_2 or HCHO can be realistically calculated from these data. The H_2O_2 data strongly suggest formation of H_2O_2 in cloud water, and that the HCHO data may be influenced by local primary emissions and possible oxidation of hydrocarbons in solution, forming HCHO.

The entire data set was also examined for correlations between H_2O_2 levels and pH. Since H_2O_2 can rapidly oxidize SO_2, lower pH values may be accompanied by reduced H_2O_2 levels because the H_2O_2 would be destroyed in the oxidation process. Figure 8 demonstrates the only storm case in which a trend between H_2O_2 levels and pH was noted. In this storm the first three samples were pH 4.5, 4.4, and 4.7, in conjunction with

H_2O_2 levels of 20, 15, and 10 ppbm respectively. In the later samples the pH ranged from 6.0-7.0 with H_2O_2 levels of 165-175 ppbm. An increase in proton concentration of 3×10^{-5} M is required for a pH drop of 2.0 units. The change in H_2O_2 concentration was from 170 ppbm to 15 ppbm or 5×10^{-6} M. If the assumption is made that the acid was produced totally through the reaction

$$H_2O_2 + SO_2 \rightarrow H_2SO_4,$$

two protons are liberated for each H_2O_2 consumed and the proton equivalent of H_2O_2 is 1×10^{-5} M. This is in reasonable agreement with the observed proton changes. Although this agreement may be fortuitous it is important to recognize that significant quantities of H_2O_2 were found in a majority of the rain samples and H_2O_2 can provide a rapid oxidant for conversion of substantial quantities of SO_2.

In a 1978 study on precipitation in the California South Coast Air Basin, Liljestrand found an average total organic carbon content of 7 ppm (36). Assuming an average HCHO content for rainwater of 200 ppbm this would indicate that HCHO comprises only 3% of the organic carbon in rainwater. He analyzed several samples for individual organic acid species and found that formic acid comprised about 17% of the organic carbon content. Coupling this with the HCHO content indicates that 13% of the carbon content is related to C_1 species.

The pH values measured in this study are exceedingly variable, ranging from a high of 8.1 to a low of 4.2. It is impossible to compare these data to those of Liljestrand because of the different sampling

techniques between the two studies. Liljestrand sampled four fractions of precipitation, the first fraction was 0.64 cm, the second and third fractions were 3.2 cm each and the final fraction was up to 21 cm of precipitation. These larger fractions collected by Liljestrand will tend to average the pH. Since the amount of buffering material in the sample also influences the pH, it is impossible to take a simple average of the data presented in this report and compare it to that of Liljestrand. The measurements of pH presented here (Appendix A) are used as references to trace pH changes, and substantial conclusions should not be drawn from them on the levels of acidity present in California South Coast Air Basin precipitation.

These measurements indicate that rainout is a major removal mechanism for HCHO. The mechanism for H_2O_2 formation and removal is uncertain. H_2O_2 levels are exceedingly variable during the course of a storm and do not follow any apparent pattern. Detailed studies on H_2O_2 levels in rain coupled with meteorological analysis will be necessary.

SECTION V

AMBIENT AIR MEASUREMENTS

The objective of this work is an examination of the spatial and diurnal variations in H_2O_2 and HCHO levels and other pollutants in the California South Coast Air Basin. The measurement program covers three years, 1979-1981. In this report data from 1979 and 1980 are presented. The spatial studies have been rather limited as the efforts have concentrated on instrument development and equipment setup.

The instrumentation used in the measurement program is detailed in Table 2. Recently some questions have arisen about the specificity of the chemiluminescent technique used for the determination of H_2O_2. The problems in the measurement of gas phase hydrogen peroxide (H_2O_2) are not with the analytical techniques for H_2O_2 but in the use of aqueous solutions for trapping gas phase H_2O_2. In aqueous solution O_3 reacts with the solution to both produce and destroy H_2O_2.

$$O_3 + H_2O \rightarrow H_2O_2 + O_2 \quad (1)$$

$$O_3 + H_2O_2 \rightarrow H_2O + 2\ O_2 \quad (2)$$

The predominance of one reaction over the other depends on the concentrations of the reactants. No relationship has been found to correlate the amount of H_2O_2 produced and the concentration of O_3 in the gas stream. Recent papers by Heikes, et. al., (37) and Zika et. al., (38) detail what is known about these reactions at this time.

In this report the H_2O_2 data presented should be considered an upper concentration limit when O_3 is present.

TABLE 2

Instrumentation Used in Ambient Air Measurements

Parameter	Instrument Model	Technique
O_3	Dasibi 1003 AH	UV absorption
NO/NO_x	Thermo Electron 14 B	Chemiluminescence
H_2O_2	HMC	Chemiluminescence
HCHO	HMC	Chemiluminescence
Temperature	EG&G 910	Platinum thermometer
Dew Point	EG&G 910	Cooled mirror
UV Radiation	Epply TUVR	Selenium cell

A. 1979 Studies

1. June - July, Claremont, California

This sampling period was characterized by moderate photochemical smog, with an O_3 maximum of ~300 ppbv. The emphasis of the measurements was on the diurnal variations in H_2O_2. The data for hourly integrated H_2O_2 samples plus selected pollutant data are given in Appendix B-1.

The data for June 13, 1979, are shown in Figure 10. Under the moderate smog conditions present the midday H_2O_2 levels of 10-15 ppbv are in line with what have been observed previously (18). The interesting feature of these data is the relatively high levels of H_2O_2 that are measured in the nighttime hours. Since the O_3 is absent, the uncertainties resulting from H_2O_2 measurements in the presence of O_3 should be removed. While the heterogeneous removal rate for H_2O_2 is unknown it is expected that in the moist evening environment of the California South Coast Air Basin removal of H_2O_2 would be rapid. This is not observed and in general H_2O_2 levels decrease much more slowly than the O_3 levels and remain at an almost constant level throughout the nighttime hours. Additional work will be necessary to detail why these seemingly high H_2O_2 levels remain throughout the night.

The next series of H_2O_2 measurements from July 24-29, 1979, shows a very similar pattern for nighttime H_2O_2. With the exception of July 29 the typical H_2O_2 levels between 00:00 and 06:00 are 2-5 ppbm. On the 29th the evening levels are much lower for some unknown reason. An examination of the data in Appendix B-1 for the other pollutant species shows no obvious differences. Another unexplained observation is the weekday/weekend differences in H_2O_2 levels. From July 24 (Tuesday) to

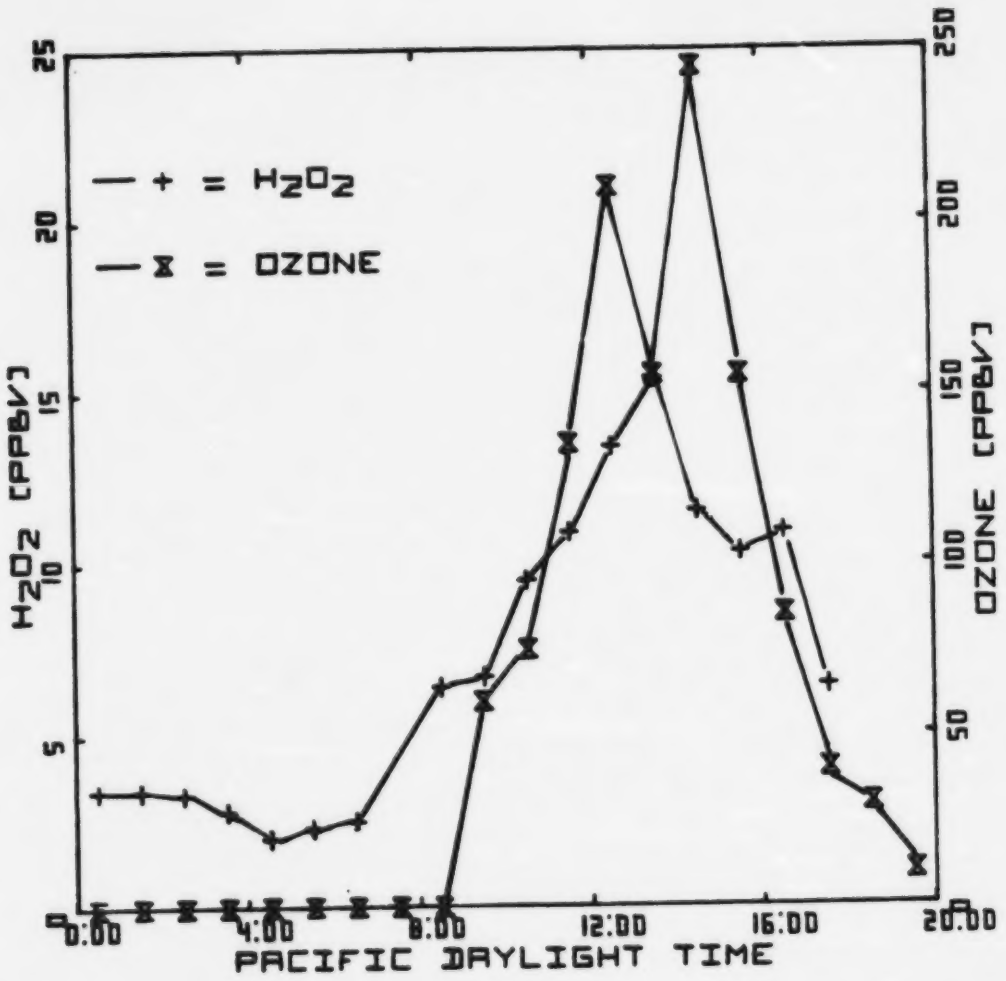


Figure 10. H_2O_2 and O_3 measurements for June 13, 1979.

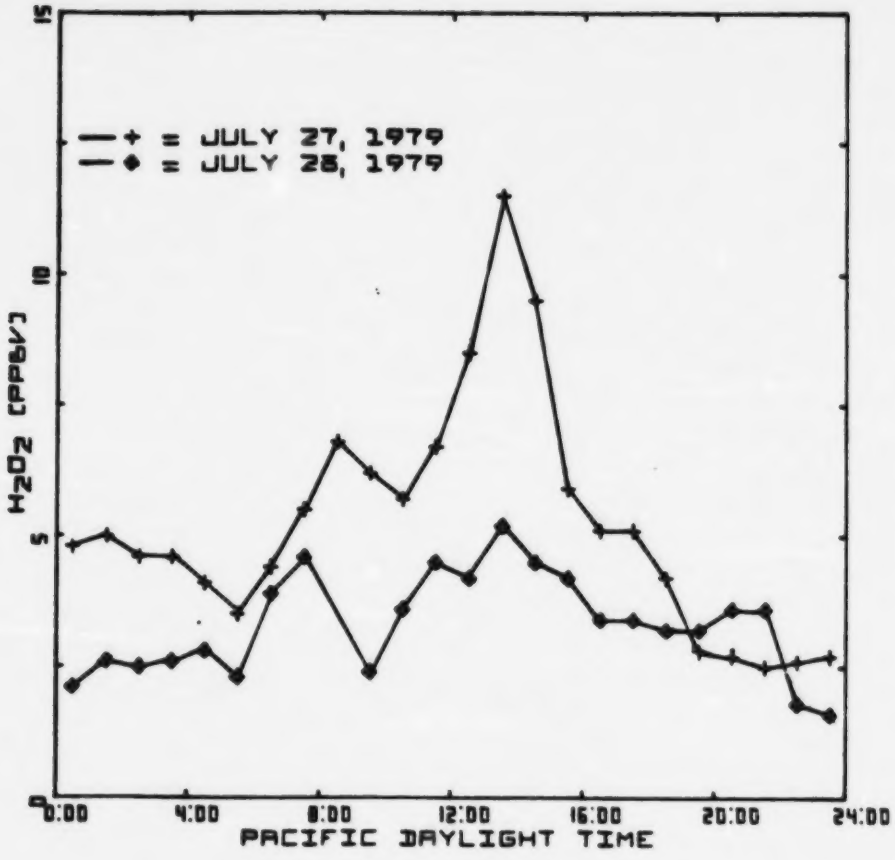


Figure 11. Measurements of H_2O_2, July 27-28, 1979.

July 27 (Friday) a well-developed maximum in the H_2O_2 concentrations is observed. The O_3 maxima during this period are relatively constant, ranging from about 250-300 ppbv. On Saturday and Sunday the O_3 and other pollutant concentrations are comparable to the weekday values, but the H_2O_2 maximum never develops. This behavior for H_2O_2 is shown in Figure 11, where the H_2O_2 data for June 27-28 are shown. At this time no explanation can be given for the reduced H_2O_2 levels.

2. Ambient Air Nitric Acid and Aerosol Nitrate Intercomparison Study, August 27 - September 3, 1979

From August 27-September 3, 1979, a field study was held at Harvey Mudd College to compare nitric acid and aerosol nitrate measurement techniques. The full data set from this study will appear as a formal EPA report (39). In conjunction with the extensive measurements of NO_x species made by other workers, measurements of H_2O_2 and HCHO were made by Harvey Mudd College personnel.

The measurement period was characterized by relatively low levels of photochemical smog and heavy overcast conditions on many of the sampling days. In terms of HCHO and H_2O_2 measurements the data are useful to view as summer "background" levels. The entire data set is given in Appendix B-2.

The H_2O_2 data shown in Figure 12 for August 30-31 are representative of those observed during this period. A reasonably strong diurnal variation is present, with generally reduced H_2O_2 levels as compared with those measured in June and July of 1979. This is probably due to the reduced levels of photochemical smog present at this time.

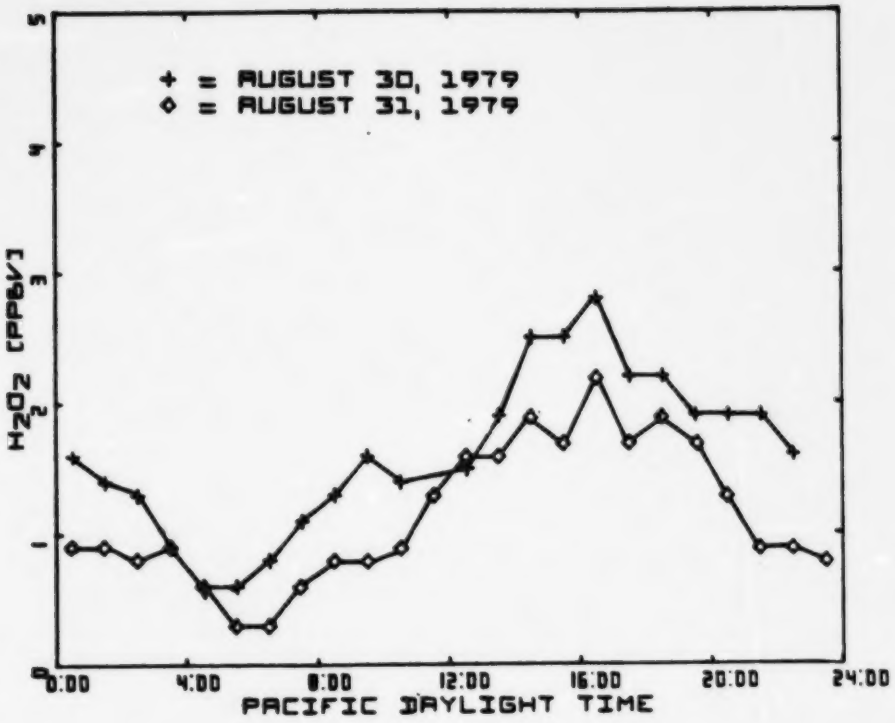


Figure 12. H_2O_2 measurements for August 30-31, 1979, Claremont, California.

The HCHO data are given in Figure 13 and can be interpreted as background levels since low amounts of photochemical smog were present. No diurnal variation in HCHO levels is evident, and the general concentration range is from 5-12 ppbv. The sampling site is sufficiently removed from local sources that traffic influences are minimal.

3. September 13-15, 1979, Claremont, California

This sampling period was during the most intense photochemical smog episode of 1979. The entire data set is given in Appendix B-3. HCHO data for two days, September 13-14, 1979, is given in Figure 14. While only four HCHO samples were taken on September 13, it is interesting to observe the early maximum in the HCHO (11:30-12:30) followed by the highest O_3 level (380 ppbv 1-hour average) of the sampling period. This early HCHO maximum is frequently observed, and discussion of it will be deferred to a later section. On September 14 the HCHO follows a more photochemical build-up and the HCHO maximum correlates in time with the O_3 maximum.

The H_2O_2 levels, shown for September 13 and 14, in figure 15 are relatively low considering the concentrations of photochemical smog present. The diurnal variations are negligible. The highest values are recorded at the start of the episode on September 13 and remain relatively constant at 1-2 ppb for the remainder of the sampling period. Potentially this is due to the high levels of photochemically generated aerosol accompanying these smog episodes, which could inhibit H_2O_2 formation or accelerate its removal.

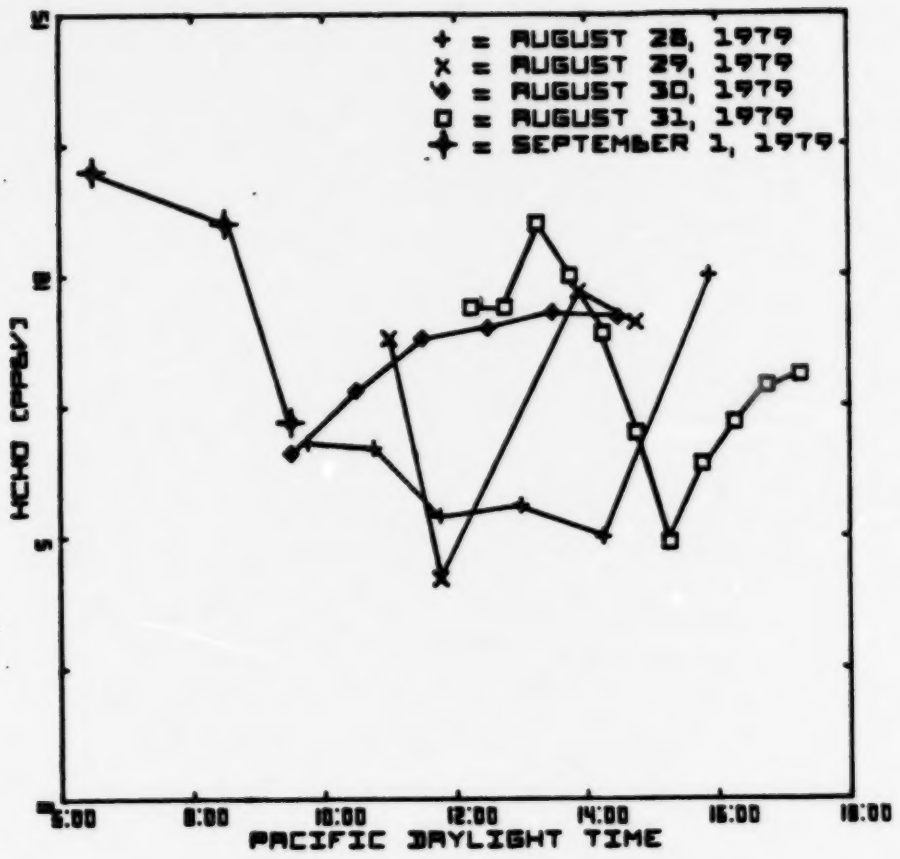


Figure 13. HCHO measurements at Claremont, California, August 28-September 1, 1979.

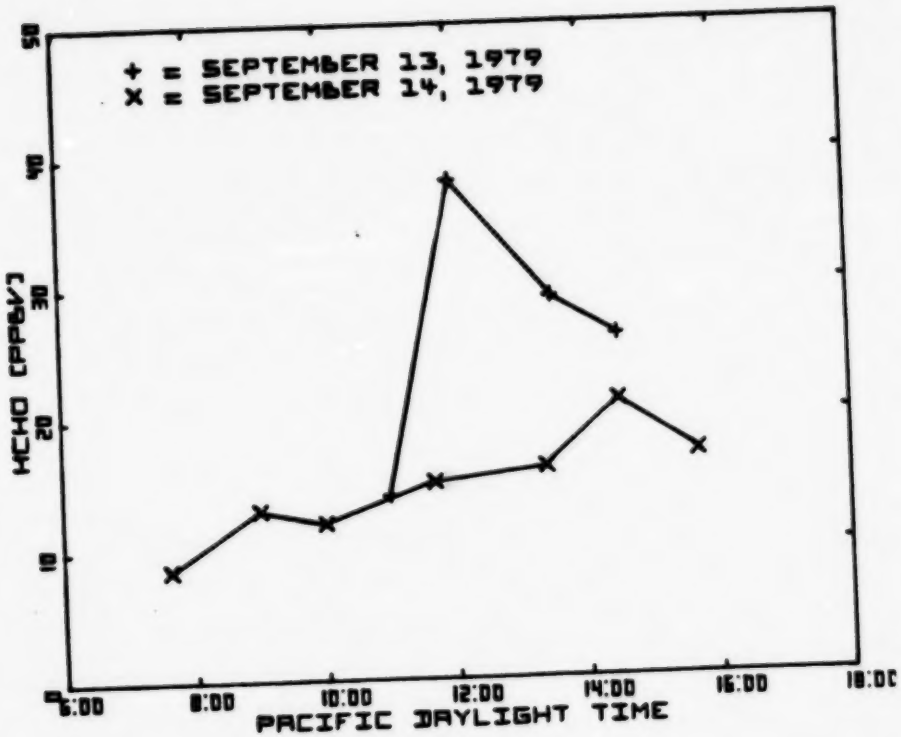


Figure 14. HCHO measurements for September 13-14, 1979.

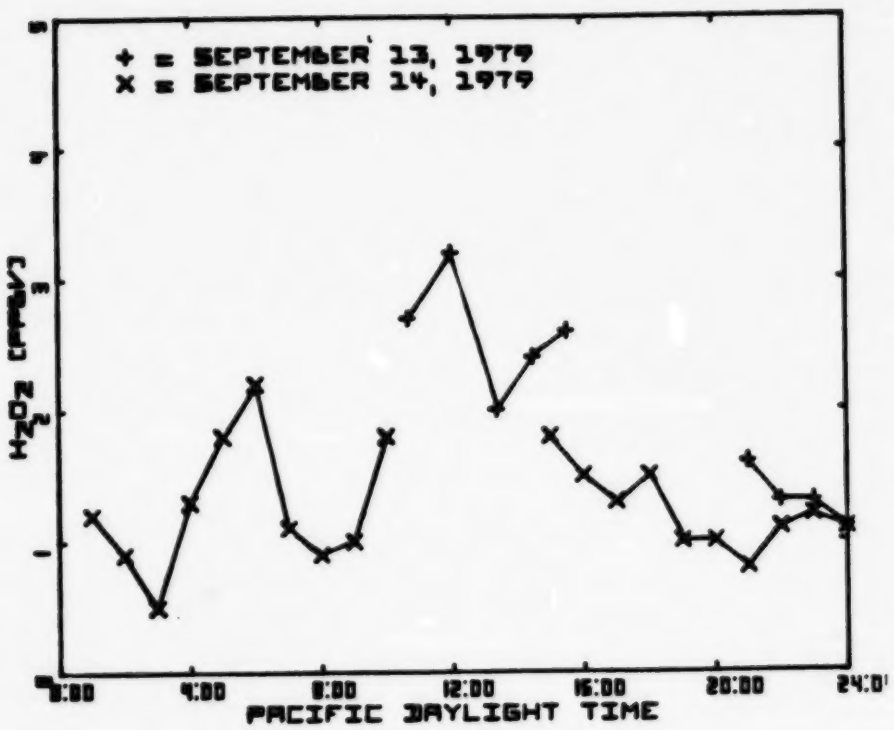


Figure 15. H_2O_2 measurements for September 13-14, 1979.

B. 1980 Studies

In 1980 four sets of ambient measurements were conducted at different locations in the California South Coast Air Basin.

1. June, California State University-Los Angeles

The first measurements were conducted June 17-20, 1980, at California State University-Los Angeles (CSLA), which is just east of the major central Los Angeles pollutant source. The measurements were conducted in conjunction with a study sponsored by the Coordinating Research Council on aldehyde method intercomparisons (32). The complete set of ambient data is given in Appendix B-4.

The CSLA sampling site is dominated by primary emissions. Ozone levels are suppressed by the large unreacted NO emissions from the central Los Angeles area. Total NO_x levels were quite high, generally averaging 100-200 ppbv. The air mass is insufficiently aged for all of the NO to be depleted by reaction with O_3.

Figure 16 shows the daytime HCHO levels for June 17-20, 1980. The data show no strong diurnal trend, and it appears that little secondary formation of HCHO has taken place since the HCHO maximum does not parallel the O_3 maximum. The major shape of the data is a broad maximum extending from 09:00-17:00 hours. This time frame corresponds to workday hours and indicates substantial primary HCHO sources. While it is impossible to precisely separate these into mobile and stationary sources it would appear that a significant function is derived from mobile sources.

It is useful to consider these data in terms of background levels and compare them with those gathered for Claremont (Figure 13) under

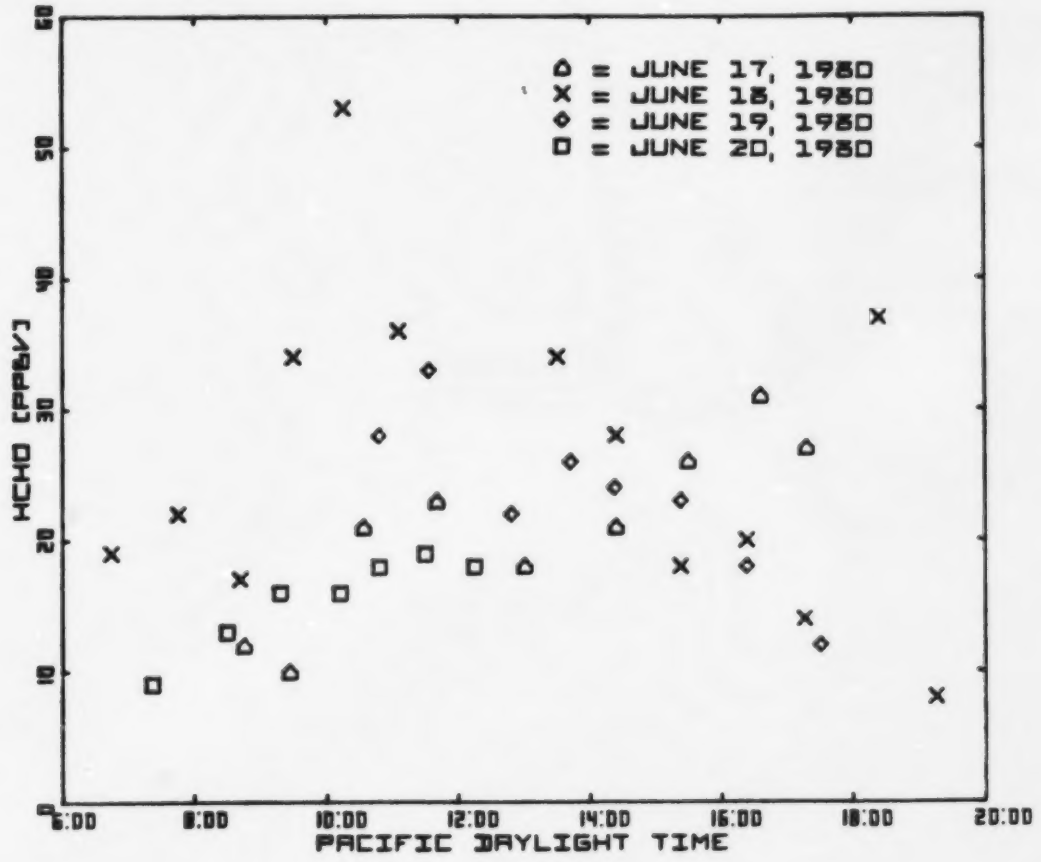


Figure 16. HCHO levels measured at California State University—Los Angeles, June 17-20, 1980.

similar conditions of low photochemistry. Considering the time period 06:00-10:00 as background, the HCHO level at CSLA averages about 15 ppbv. The daytime background is higher, averaging about 25 ppbv. The wind trajectories show that a majority of the pollutants measured at the CSLA site would be transported north into mountains rather than east into the basin (40). For the Claremont site the major source of pollutants is the southern part of Los Angeles and Long Beach. Since lower background levels of HCHO appeared at Claremont under generally similar photochemical conditions it would appear that lower less primary emissions of HCHO take place in the southern Los Angeles-Long Beach area.

Two days of H_2O_2 measurements can be analyzed. These are for June 18 and 19, 1980. The data are shown in Figure 17. A general trend of the H_2O_2 levels decreasing during the day is apparent with a sharp drop between 15:00-16:00 on June 18. In an examination of the other data no sharp changes in concentrations are noted during this time period. In comparison with the 18th June 19 shows generally higher concentrations with the same type of decrease in the evening hours. The daily trends for H_2O_2 concentrations follow those for ozone with the average H_2O_2 on June 19 being much higher than the 18th, corresponding to maximum hourly O_3 concentrations of 194 and 136 ppbv, respectively. These data also show the H_2O_2 levels dropping off much less sharply than the O_3 levels.

2. September 11-12, Palo Verde, California

Sampling of pollutants at a coastal location was conducted on September 11-12 at Point San Vicente located on the Palo Verde Peninsula. The objective was to examine what pollutants would be present in the air masses that flow into the CSCAB area.

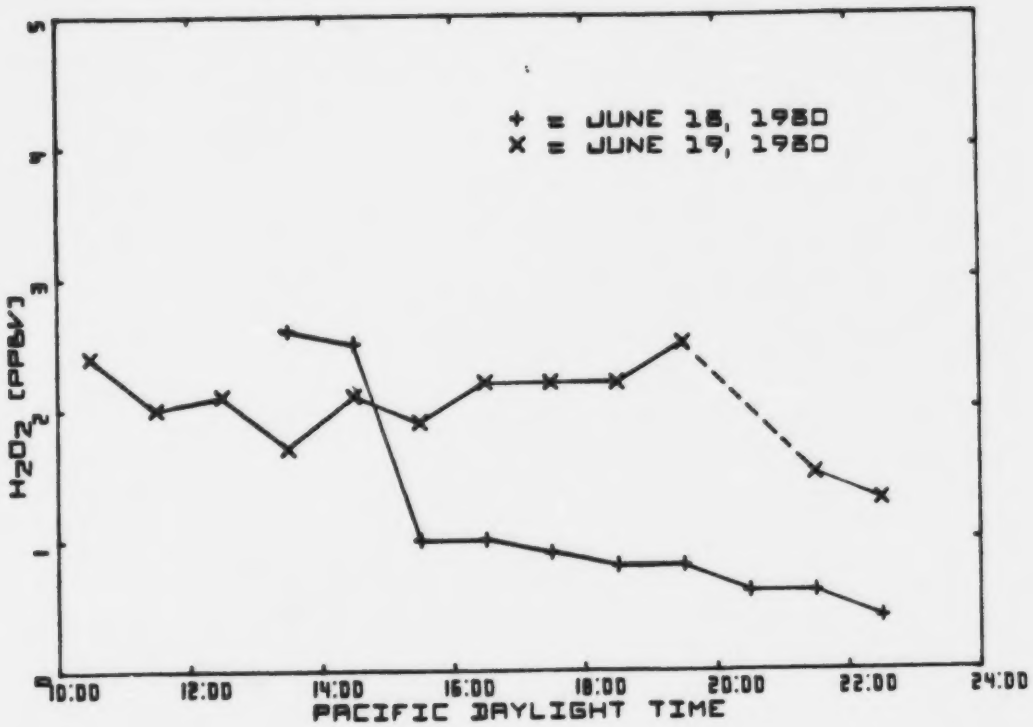


Figure 17. H_2O_2 levels measured at California State University, Los Angeles, June 18-19, 1980.

The sampling period was characterized by a modest inverstion in the basin area and relatively low wind velocities at the sampling site. The data set for the measured pollutants is given in Appendix B-5. The HCHO and H_2O_2 data are shown in Figure 18. The most unique feature of this data is the relatively high levels of HCHO and H_2O_2 measured. No data are available on clean air levels of H_2O_2, but an extensive study on HCHO over the ocean showed maximum levels to be between 2-3 ppbv (41). For a majority of the sampling period the HCHO levels are nearly an order of magnitude higher than this. They also show a strong correlation with direction of the incoming wind. In the early part of the sampling the air flow is directly onshore (wind from the west) and the HCHO levels are the lowest. As the wind shifts to the northwest the HCHO levels increase slightly. This indicates that the air flow, which is still directed onshore, has had prior contact with urban areas. The most dramatic correlation between HCHO and wind is from 04:00-06:00. During this time the wind flow is largely offshore and originates in the Long Beach-San Pedro refinery area. The sampling conducted during this time gives very high HCHO levels. As the wind shifts in the subsequent hours the HCHO levels drop. The important consideration is that the air flow directed onshore contains nearly 20 ppbv of HCHO. This very elevated level of HCHO is enough to accelerate photochemical smog production.

The H_2O_2 levels measured at this site are relatively high compared with the measurements made in the basin during 1980. The H_2O_2 levels show somewhat of a diurnal variation, but it is difficult to predict the exact shape from the limited data set.

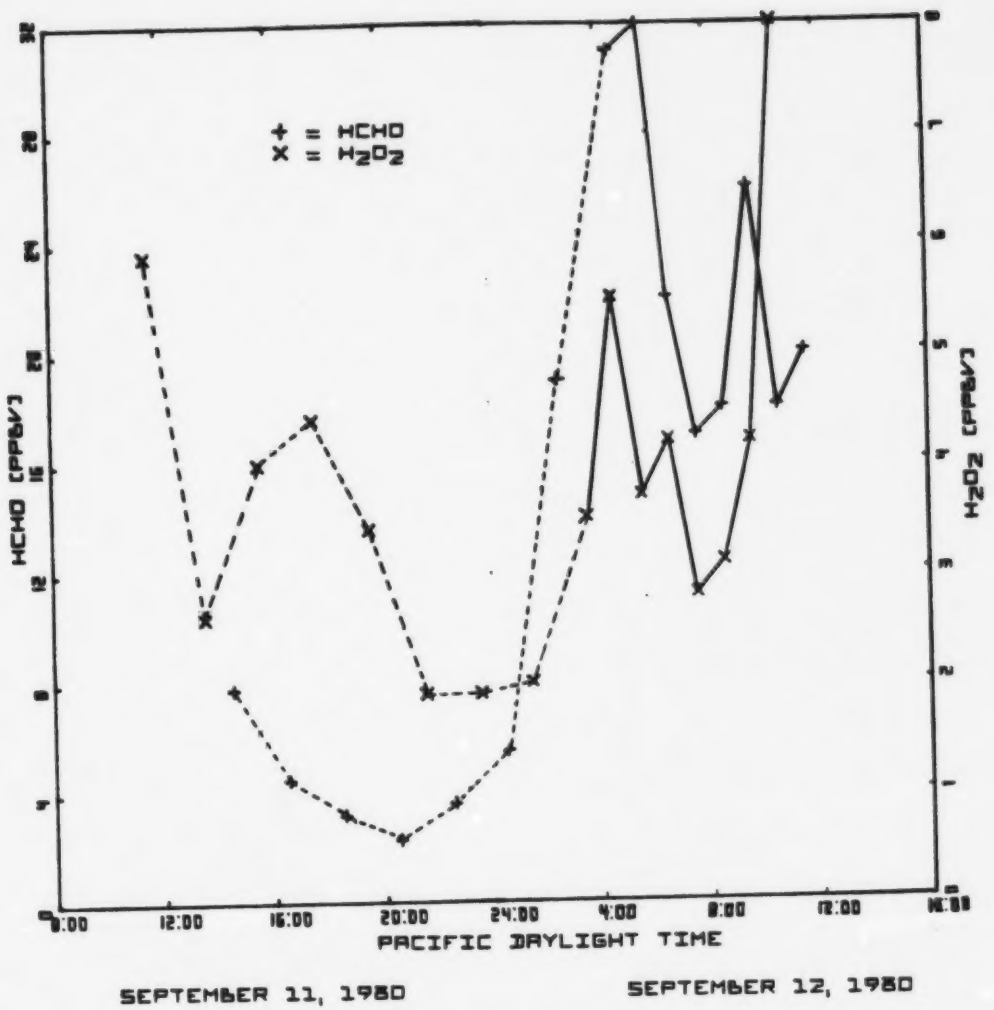


Figure 18. Measurements of HCHO and H_2O_2 at Palos Verdes, California, September 11-12, 1980.

These measurements are the first known measurements of HCHO and H_2O_2 at a coastal site in the CSCAB. The relatively high levels of both species found when the air flow is onshore suggest that transport of of these species into the basin could provide reasonable quantities of photoinitiators for photochemical smog production.

3. September-October, Claremont, California

Ambient air sampling was conducted from Claremont as part of the fall phase of the CRC-sponsored aldehyde study. The measurement period was characterized by intense photochemical smog with two of the sampling days having hourly ozone maxima in excess of 400 ppbv. The entire data set of this episode is given in Appendix B-6. No NO_x data are presented in this data set but detailed NO, NO_2, HNO_3, and PAN measurements for the same period can be found elsewhere (42, 43). This data set has the potential of being one of the most complete chemical data sets ever assembled for modeling purposes since diurnal measurements of such diverse species as aldehydes (both HCHO and higher species) and nitric acid are available for the same sampling location. The present analysis will concentrate on the aldehyde and H_2O_2 data.

The sampling period was characterized by an intense photochemical smog episode of the type that frequently builds in the fall during September and October. These episodes are characterized by a strong inversion layer that does not lift completely during the evening hours. The aged pollutants from the preceding day remain in the basin and help to accelerate photochemical smog formation.

The HCHO values measured by the CL technique are low compared with the parallel aldehyde measurements made by the HPLC technique and expected

HCHO levels for photochemical smog of this magnitude based on previous experience. The CL HCHO data appear to have a proportional interference, because the data show a diurnal variation similar to that of the HPLC and CA techniques, but the CL data are low by an approximate factor of 3. The source of this interference is unknown.

The first episode to be examined is September 25-26, 1980. This period was characterized by heavy photochemical smog, with an O_3 maximum of $\sim$350 ppb. The measurements were made during a 36-hour block involving aldehydes, H_2O_2, and other supporting measurements. The HCHO levels measured by CL and HPLC are shown in Figure 19. The O_3 and H_2O_2 data are given in Figure 20.

Measurements of H_2O_2 during this period are surprisingly low, with a maximum of 1.8 ppbv. This is in sharp contrast to other smog episodes, where H_2O_2 levels of 10-20 ppbv have been routinely measured. The H_2O_2 levels track with the O_3 concentrations. An interesting feature of this data is the very low levels measured in the evening hours. Possibly this is due to the heavy inversion and the build-up of organic species that could react with H_2O_2. These data are in sharp contrast to those obtained at Claremont in June-August of 1979 or at Palo Verde in September of 1980.

The second major smog episode occurred October 1-2, 1980. On October 2 the O_3 hourly averages were above 400 ppbv for 2 hours. The HCHO measurements by CL and HPLC and the O_3 data are shown in Figure 21. On October 1 the O_3 maximum lags the HCHO maximum by several hours, while on October 2 a double HCHO maximum is present preceding the O_3 maximum. Even more surprising is the fact that on October 2 the HCHO

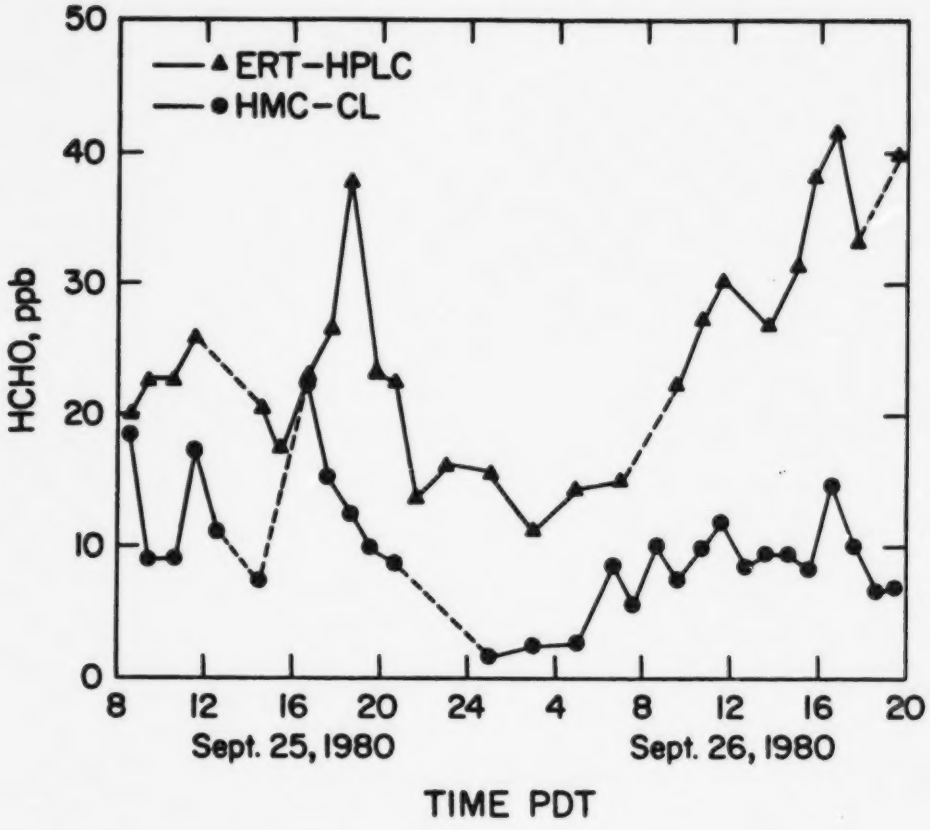


Figure 19. Ambient air measurements of HCHO by HPLC and CL, September 25-26, 1980.

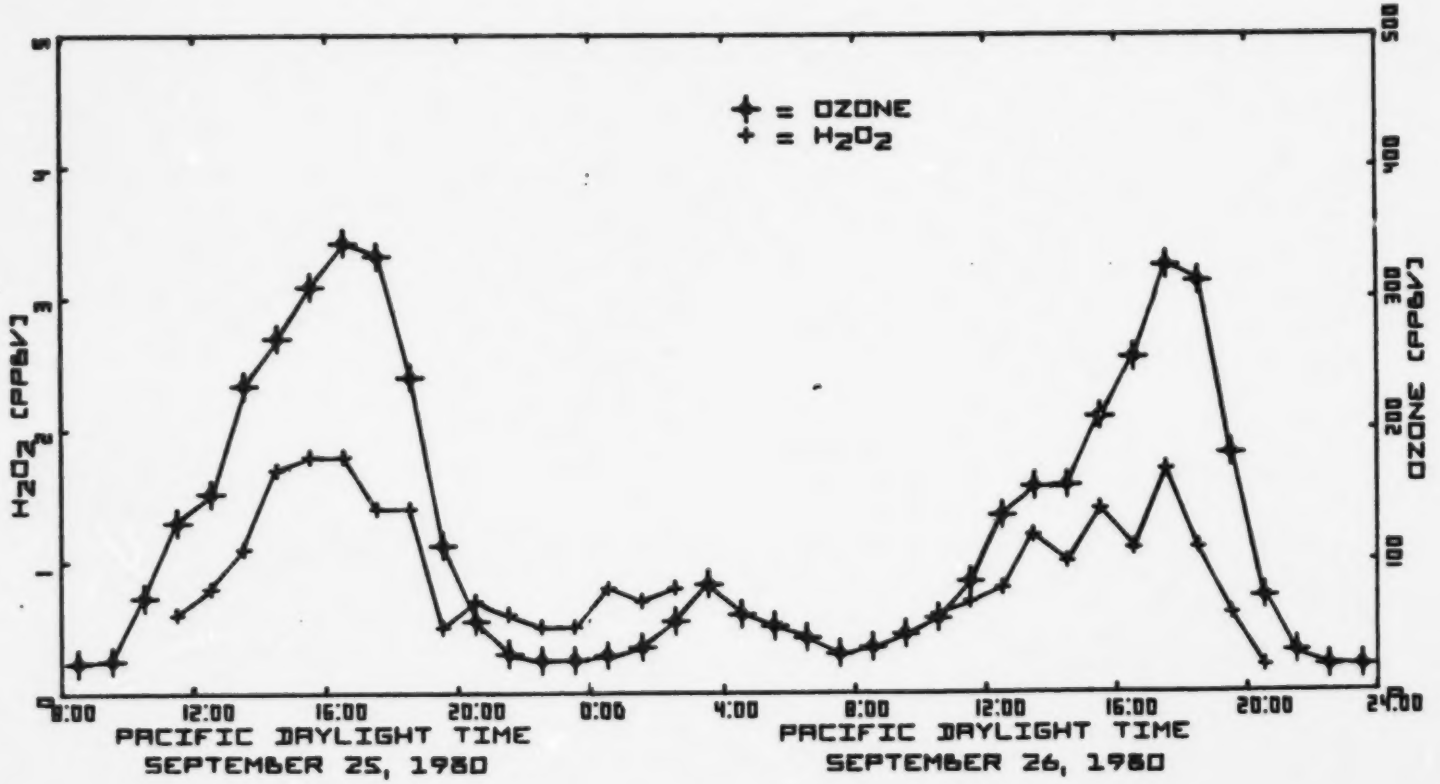


Figure 20. Levels of O_3 and H_2O_2 measured at Claremont, California, September 25-26, 1980.

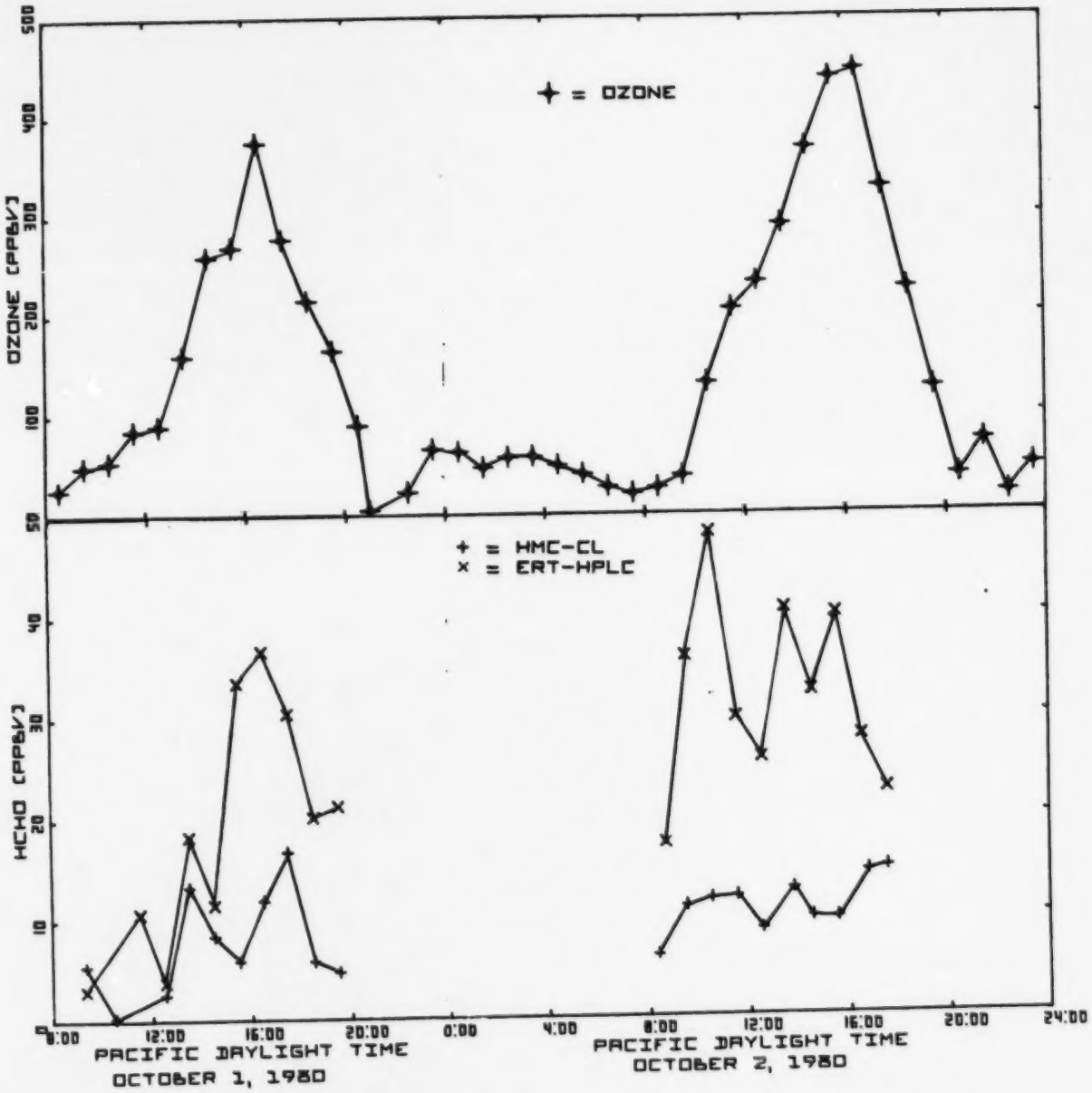


Figure 21. Measurements of HCHO by HPLC and CL and O_3 data for October 1-2, 1980 at Claremont, California.

maximum occurs between 10:00 and 11:00 hours and is followed by a second slightly smaller maximum 3 hours later.

The observation of the maximum in HCHO concentrations in the mid-morning hours is quite frequent, and it is generally followed by a high O_3 maximum. Presumably this condition is brought about by a high concentration of alkenes in the early morning hours that can react with the O_3 produced to generate HCHO. The HCHO can then accelerate the photochemistry and lead to increased O_3 production. The link between HCHO and O_3 has been well established in smog chamber studies (44), and these results are the first atmospheric studies that indicate this relationship. More extensive studies on air trajectories will be necessary to amplify on this observation.

As part of this study filter samples were collected to determine the aldehyde content of the aerosol phase. Samples were collected on Teflon filters, (Millipore FALP, 1 μm pore size, 47 mm diameter) for four hours at a flow rate of approximately 20 l-liters per minutes. The filters were cut in half at the end of this period and analyzed by the CL and HPLC technique.

The only other known measurements of aerosol HCHO have been made by Klippel and Warnek in Germany (20, 45). These workers found that approximately 1% of the total HCHO content of the atmosphere was present in the aerosol phase. They made most of these measurements at coastal locations in clean air masses.

The HCHO data for nine filter samples is given in Appendix B-6-20. In eight of the nine samples the CL technique gave higher values than the HPLC technique. This is a useful observation since in the measurement of gas-phase HCHO the HPLC technique was uniformly higher by a factor of

2 to 3. The interferant which caused the lower HCHO values measured by CL must not have been collected on the filters since the aerosol HCHO values are comparable with the CL slightly higher.

The diurnal variation in aerosol HCHO is relatively small, less than a factor of two. Because of the differences in gas-phase and aerosol measurements between the two techniques, ranges can only be given for the gas/aerosol HCHO ratios. At the midday HCHO maximum approximately 1% of the HCHO is aerosol, and in the evening hours this increases to about 5%. Since the condensed phase chemistry of HCHO is very complex it is impossible to calculate any theoretical values for this partition. It is possible that the aerosol phase becomes enriched in HCHO in the evening hours. Formaldehyde is water soluble, and it is possible with the elevated humidity in the evening that considerable HCHO may dissolve in the aerosols. Addition compounds of HCHO with a variety of species are well known, and these will be favored at lower temperatures. Thus the aerosol phase could act as a reservoir for gas-phase HCHO in the evening hours and liberate HCHO as the temperature rises.

The present data are too limited to draw any major conclusions. It would appear that aerosol HCHO is sufficiently limited that no precautions need to be taken to avoid bias in the sampling for gas-phase HCHO. Any measurements will need to include data on total aerosol concentration and water content of the aerosols.

4. Measurements in Downtown Los Angeles

On November 13, 1980, measurements of HCHO were made at street level, near the corner of 6th and Hill in central Los Angeles. The

objective of this study was to examine the HCHO exposure levels for pedestrian traffic presuming large influences from vehicular emissions. The data are given in Appendix B-7 and figure 22. The meteorology can be characterized as typical for the fall with a low mixing height and little wind in the morning, with the mixed layer increasing during the day. Local vehicle traffic is relatively constant throughout the day, and so no rush hour impacts would be expecte

The relatively regular decrease of HCHO during the day suggests that the dominating factor for HCHO levels is the height of the mixed layer under these sampling conditions. The levels measured here on November 13, 1980, are considerably less than those recorded by Altshuller and McPherson (10) and Altshuller et al. (11) in September of 1961. This trend of lower HCHO levels is in general agreement with the observations made in the introduction. Presumably the HCHO values measured here represent the lower concentrations that will be encountered. During the summer months, which have more stable inversion layers and potential for some secondary HCHO formation, the HCHO concentrations could be increased.

C. Summary

Since this set of data is the largest compilation of HCHO and H_2O_2 measurements, it is useful to look at the relationships between the intensity of photochemical smog and the concentrations of HCHO and H_2O_2. In Figure 23 all of the HCHO/O_3 data for Claremont has been assembled. This plot is the maximum HCHO data on a given day and the maximum O_3 concentration. Since HCHO is both an initiator and product of photochemical reactions the hourly average maximums for each species were taken even if they occurred at different times.

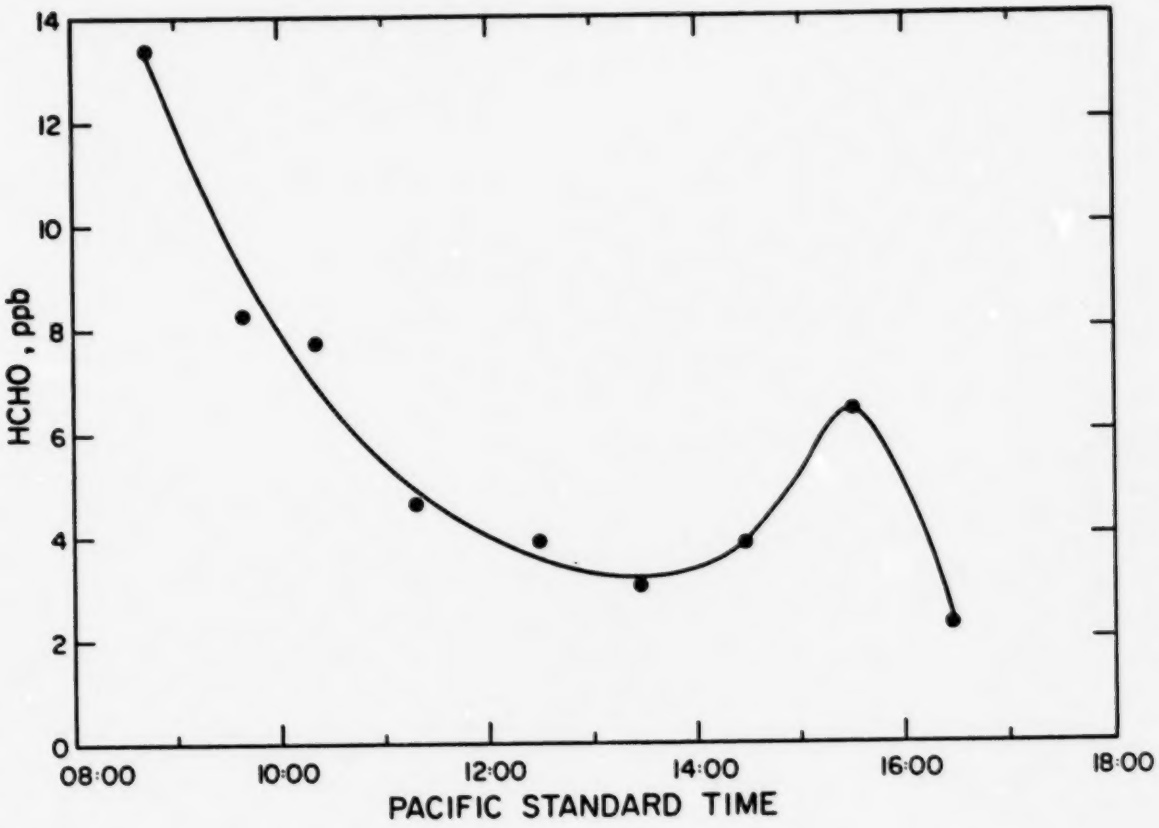


Figure 22. Levels of HCHO measured in downtown Los Angeles, November 13, 1981.

In spite of the diversity in measuring techniques and meteorology that accompany these measurements, a reasonable trend is apparent in Figure 23. An almost linear relationship is seen in the points indicated with the pentagonal symbol. These data would be expected to give the best relationship since they were gathered over a period of five consecutive days and tend to minimize meteorological variations.

At the lower O_3 concentrations a baseline level of about 10 ppbv is observed resulting from primary emissions. As the daily maximum HCHO level increases, the O_3 level increases also. Qualitatively the ambient data shown are in Figure 23 very similar to those of Pitts et al. in smog chamber simulations with added HCHO (44).

The relationships between H_2O_2 concentrations were recorded at the time of the O_3 maximum. No distinct trends are apparent as seen in Figure 24, but it would appear that at midrange O_3 concentrations, 250-350 ppbv, the H_2O_2 concentrations reach a maximum and that lower levels are present for either higher or lower concentrations of O_3. Since H_2O_2 can be easily destroyed by heat or particle surfaces it is not unexpected that a complex behavior will be present. Detailed modeling efforts will be necessary to detail the atmospheric chemistry of H_2O_2.

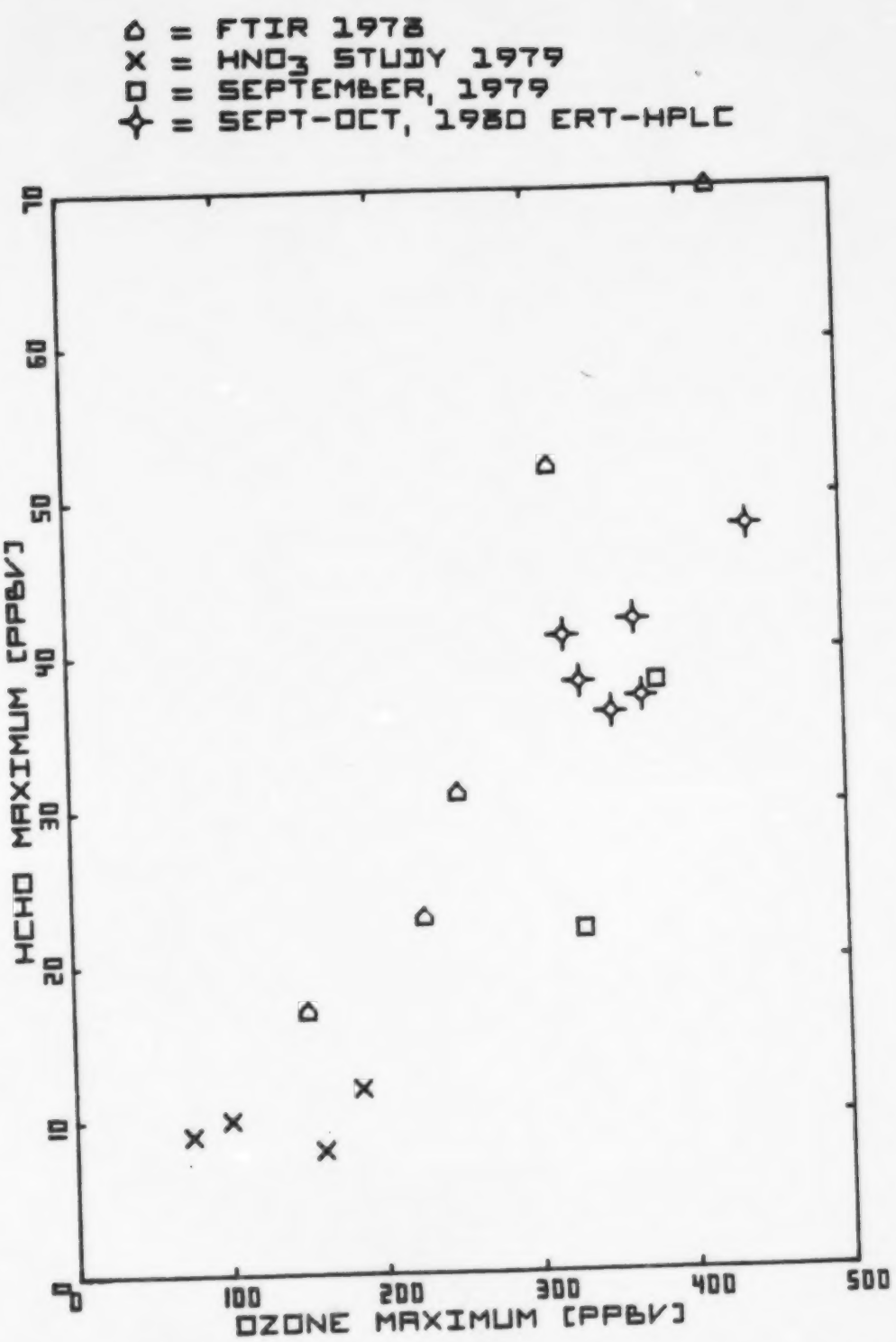


Figure 23. Summary of HCHO measurements made at Claremont, California from 1978-1980

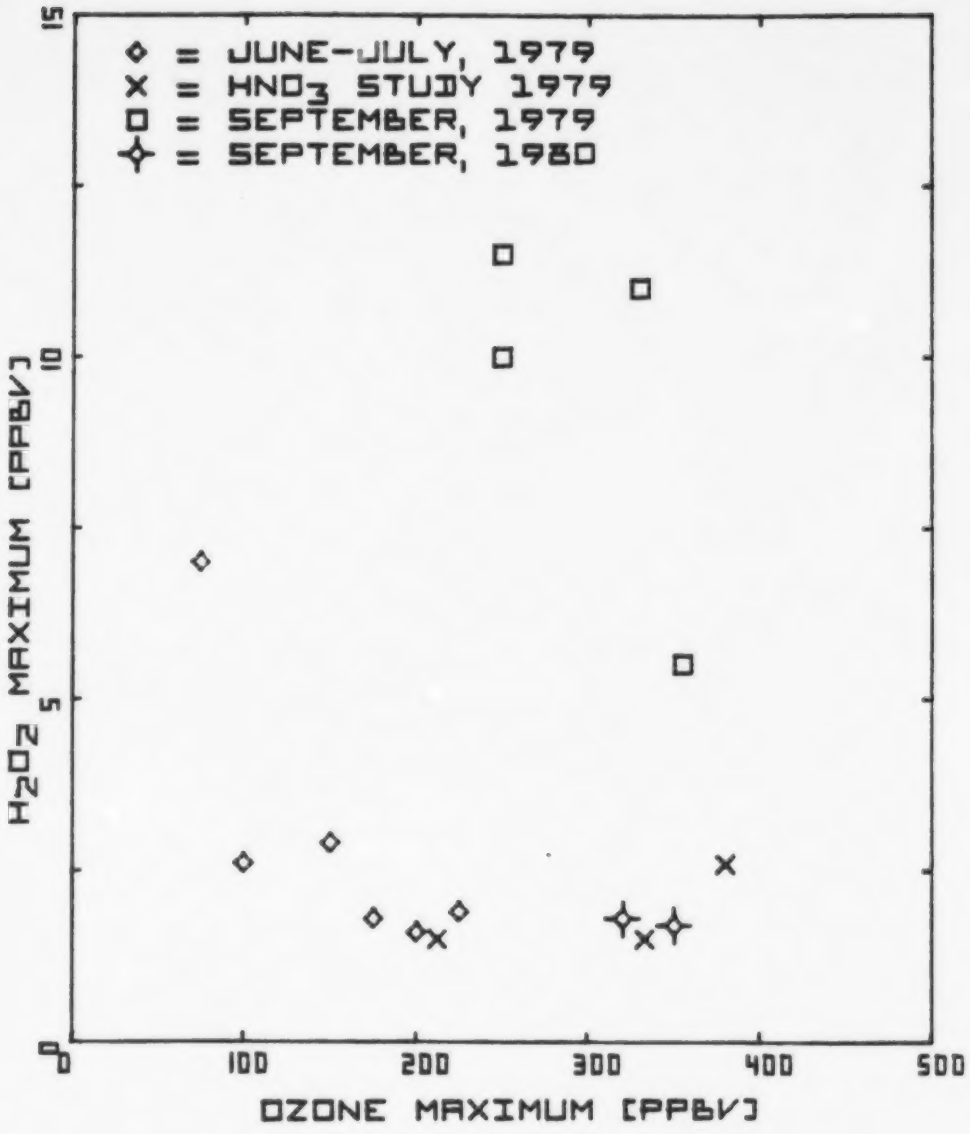


Figure 24. Summary of H_2O_2 measurements made at Claremont, California in 1979 and 1980.

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APPENDIX A

TABLE A-1. HCHO and H_2O_2 Concentrations in Rain. January 27-29, 1980, Claremont, California.

Sample No.	Time	pH	HCHO ppbm	H_2O_2 ppbm	Comments
1	-23:00	6.2	670	130	1/27/80 Samples 1-54 =
2	23:00-00:00	6.3	335	170	1/28/80 0.8 mm precip.
3	00:00-01:00	6.4	145	115	each
4	01:00-02:00	6.2	75	55	
5	02:00-02:30	6.1	90	70	
6	02:30-03:00	6.1	60	65	
7	03:00-04:00	6.6	50	30	
8	04:00-05:00	6.9	45	65	
9	05:00-06:00	6.2	35	60	
10	06:00-06:30	6.3	60	105	
11	06:30-07:00	6.1	55	60	
12	07:00-07:50	5.2	45	75	
13	07:50-08:00	5.4	90	20	
14	08:00-08:15	5.3	50	10	
15	08:15-08:30	5.8	115	40	
16	08:30-08:35	5.5	85	60	
17	08:35-09:15	4.7	75	170	
18	09:15-10:05	5.1	55	115	
19	10:05-10:10	5.2	75	95	
20	10:10-10:15	5.5	110	45	
21	10:15-10:20	5.9	120	60	
22	10:20-10:23	5.4	65	620	
23	10:23-10:25	5.9	65	665	
24	10:25-10:30	6.0	90	430	
25	10:30-10:31	6.0	30	125	
26	10:31-10:36	6.2	80	110	
27	10:36-10:38	6.2	60	335	
28	10:38-10:40	6.1	65	160	
29	10:40-10:41	6.2	65	135	
30	10:41-10:42	6.3	40	85	
31	10:42-10:43	6.2	55	25	
32	10:43-11:00	6.2	35	50	
33	11:00-13:00	6.1	90	25	
34	13:00-15:25	6.0	220	415	
35	15:25-15:27	4.8	90	575	
36	15:27-15:29	4.7	130	380	
37	15:29-15:30	4.6	130	315	

TABLE A-1. (continued) - 2

Sample No.	Time	pH	HCHO	H_2O_2	Comments
38		4.8	ND[a]	250	
39		4.7	ND	250	
40		4.6	380	ND	
41		5.4	ND	250	
42		4.9	ND	150	
43		4.5	ND	110	
44		4.2	ND	120	
45		4.7	ND	90	
46		4.6	ND	115	
47		4.5	ND	55	
48		6.4	ND	55	
49		6.5	ND	50	
50		6.2	ND	40	
51		6.4	ND	20	
52		6.2	ND	20	
53		6.4	ND	ND	
54		6.3	30	ND	
55	17:15-18:00	6.2	35	ND	Samples 55-60 = 1.1 mm
56	18:00-19:00	5.9	20	25	precip. each
57	19:00-02:00	5.7	15	25	
58	20:00-21:00	5.6	25	20	
59		ND	ND	ND	
60		ND	ND	ND	
61	22:45-23:00	5.8	ND	35	Samples 61-84 = 1.3 mm
62	23:00-20:00	6.1	50	20	1/29/80 precip. each
63	00:00-01:00	6.2	50	30	
64	01:00-02:00	5.7	55	35	
65	02:00-03:00	5.6	50	45	
66	03:00-04:00	5.5	35	40	
67	04:00-05:55	6.0	65	0	
68	06:00-06:10	6.3	35	45	
69	06:10-06:15	6.5	30	80	
70	06:20-06:30	6.5	30	80	
71	06:30-07:00	6.5	55	80	
72	07:00-08:00	6.7	40	50	
73		6.3	45	85	
74		6.5	30	50	
75		6.1	20	50	
76		6.2	ND	60	
77		6.7	ND	110	
78		6.6	ND	110	
79		6.7	ND	140	
80		6.0	ND	300	
81		6.2	ND	75	

TABLE A-1. (continued) - 3

Sample No.	Time	pH	HCHO	H_2O_2	Comments
82		6.6	ND	80	
83	07:30	6.5	ND	80	
84	22:00-05:00	4.6	185	160	1/30/80

[a]ND = No Data.

TABLE A-2. HCHO and H_2O_2 Concentrations in Rain. February 13-15, 1980, Claremont, California.

Sample No.	Time	HCHO ppbm	H_2O_2 ppbm	Comments
1	07:45-08:44	670	210	2/13/80
2	08:44-10:58	480	375	Samples 1-28 = 0.6 mm
3	10:58-11:10	345	200	precip. each
4	11:10-11:22	250	60	
5	11:22-11:27	145	35	
6	11:27-11:32	70	15	
7	11:32-11:51	ND[a]	15	
8	11:51-12:01	90	25	
9	12:01-12:10	ND	35	
10	12:10-12:20	ND	30	
11	12:20-12:27	ND	35	
12	12:27-12:37	ND	40	
13	12:37-12:44	ND	55	
14	12:44-12:48	ND	35	
15	12:48-12:50	ND	35	
16	12:50-12:55	ND	25	
17	12:55-13:00	ND	45	
18	13:00-13:10	ND	45	
19	13:10-13:16	ND	30	
20	13:16-13:28	ND	10	
21	13:28-13:36	ND	40	
22	13:36-13:46	ND	210	
23	13:46-13:56	ND	60	
24	13:56-14:24	ND	100	
25	14:24-14:35	ND	75	
26	14:34-14;35	ND	95	
27	14:35-14:44	ND	125	
28	14:44-14:54	ND	120	Samples 29-40 = 0.8 mm
29	14:54-15:35	ND	120	precip. each
30	15:35-15:54	ND	345	
31	15:54-16:13	ND	380	
32	16:13-16:56	ND	210	
33	16:56-17:15	ND	275	
34	17:15-19:00	105	440	
35	19:00-19:55	ND	310	
36	19:55-20:19	ND	130	
37	20:19-20:28	ND	100	
38	20:28-20:37	75	45	
39	20:37-20:47	60	65	Samples 40-95 = 1.1 mm
40	20:47-21:06	ND	65	
41	21:06-22:06	ND	ND	
42	22:06-22:25	95	ND	
43	22:25-22:44	ND	ND	

TABLE A-2. (continued) 2

Sample No.	Time	HCHO ppbm	H_2O_2 ppbm	Comments
44	22:44-23:02	ND	ND	
45	23:02-23:18	50	ND	
46	23:18-23:32	ND	ND	
47	23:32-00:03	ND	ND	2/14/81
48	00:03-00:22	ND	ND	
49	00:22-00:46	ND	ND	
50	00:46-01:05	80	55	
51	01:05-01:23	40	ND	
52	01:23-01:37	ND	ND	
53	01:37-01:47	ND	ND	
54	01:47-02:11	ND	ND	
55	02:11-03:11	ND	ND	
56	03:11-05:06	ND	55	
57	05:06-07:16	105	ND	
58	07:16-07:36	90	ND	
59	07:36-11:02	200	ND	
60	11:02-14:06	125	ND	
61	-20:01	530	500	
62	20:01-21:20	85	ND	
63	21:20-21:34	50	120	
64	21:34-21:44	80	375	
65	21:44-21:58	ND	540	
66	21:58-22:56	ND	325	
67	22:56-23:30	40	ND	
68	23:30-23:39	50	560	
69	23:39-23:59	60	ND	
70	23:59-01:04	ND	400	
71	01:04-01:10	45	ND	2/15/80
72	01:10-01:30	ND	815	
73	01:30-02:59	ND	ND	
74	02:59-03:29	ND	340	
75	03:29-03:59	47	ND	
76	03:59-04:09	ND	375	
77	04:09-04:44	ND	ND	
78	04:44-05:08	55	590	
79	05:08-05:51	ND	ND	
80	05:51-06:36	ND	333	
81	06:36-06:41	ND	ND	
82	06:41-07:48	70	530	
83	07:48-07:55	ND	ND	
84	07:55-08:43	75	65	
85	08:43-08:57	ND	40	
86	08:57-09:11	ND	75	
87	09:11-09:14	ND	ND	

TABLE A-2. (continued) 3

Sample No.	Time	HCHO ppbm	H_2O_2 ppbm	Comments
88	09:14-09:24	ND		Intense rain shower
89	09:24-09:34	55	100	
90	09:34-09:44	ND	150	
91	09:44-10:17	85	ND	
92	10:17-10:58	120	75	
93	10:58-12:00	ND	ND	
94	12:00-16:38	185	45	

[a] ND = no data.

TABLE A-3. HCHO Concentrations in Rain. January 27-29, 1981, Claremont, California.

Sample No.[a]	HCHO ppbm	Comments
1	235	Rain began 21:30, 1/27/81
2	220	
3	210	Steady drizzle
4	90	
5	40	
6	49	07:00, 1/28/81
7	85	Steady drizzle
8	90	
9	100	08:30
10	95	
11	270	09:45 rain terminated briefly
12	340	11:45 heavy rain

[a] Each sample is 2.2 mm of precipitation.

TABLE A-4. HCHO and H_2O_2 Concentrations in Rain. January 28-29, 1981, Claremont, California.

Sample No.[a]	Time	HCHO ppbm	H_2O_2 ppbm	Comments
1	16:00	730	20	2/28/81 hail for 5 min, pH 4.5
2	18:00	479	15	Thunder 17:30-18:00, pH 4.4
3	18:30	185	10	pH 4.7
4		240	165	pH 6.0
5		100	175	pH 6.6
6	10:00	100	175	2/29/81 pH 7.0
7		90	170	
8		65	110	
9		70	220	
10		85	240	
11	12:30	55	145	
12		50	70	
13		100	45	
14		40	70	
15		45	35	
16		45	50	
17	13:20	30	ND[b]	

[a] Each sample is 1.4 mm of precipitation.

[b] ND = no data.

TABLE A-5. HCHO and H_2O_2 Concentrations in Rain. February 8-9, 1981, Claremont, California.

Sample No.[a]	pH	HCHO ppbm	H_2O_2 ppbm	Comments
1	7.2	540	770	Rain began 18:00, 2/8/81
2	6.2	160	700	
3	6.4	250	290	
4	6.2	275	250	
5	6.1	250	710	
6	5.8	345	220	
7	5.6	115	10	
8	5.3	70	ND[b]	
9	5.5	45	15	
10	5.4	95	80	
11	5.3	30	100	
12	5.2	35	55	
13	5.0	80	ND	
14	5.0	73	220	
15	5.6	20	25	Rain ended 15:00, 2/9/81

[a] Eeach sample is 1.4 mm of precipitation.

[b] ND = no data.

TABLE A-6. HCHO and H_2O_2 Concentrations in Rain. February 25-26, 1981, Claremont, California.

Sample No.[a]	pH	HCHO ppbm	H_2O_2 ppbm	Comments
1	5.7	60	180	Rain began 18:00, 2/25/81
2	8.1	30	160	
3	6.3	25	110	
4	6.2	20	80	
5	6.8	15	30	
6	5.8	30	35	
7	6.5	40	45	
8	5.6	60	35	
9	4.6	105	15	Rain ended 05:00, 2/26/81

[a] Each sample is 1.4 mm of precipitation.

TABLE A-7. HCHO Concentration in Rain. March 19-20, 1981, Claremont, California.

Sample No.[a]	Time	pH	HCHO ppbm
1	14:00-16:48	4.7	200
2	16:48-17:00	5.0	75
3	17:00-17:10	5.0	30
4	17:10-17:19	5.2	40
5	17:19-17:29	5.0	105
6	17:29-17:36	5.6	105
7	17:35-17:44	5.8	30
8	17:44-17:55	6.2	40
9	17:55-18:07	5.8	40
10	18:07-18:51	5.9	80
11	18:51-18:59	5.8	30
12	18:59-19:28	6.0	70
13	19:28-20:05	5.2	60
14	20:05-20:15	5.2	130
15	20:15-20:39	4.9	50
16	20:39-01:48	4.5	75
17	01:48-02:15	4.9	60

[a] Each sample is 1.4 mm of precipitation.

APPENDIX B

AMBIENT AIR MEASUREMENTS

All data unless otherwise indicated are given in terms of hourly averages with the period ending at the time listed.

TABLE B-1. Ambient Air Measurements, June 13, 1979, Claremont, California.

Time PDT	H_2O_2	O_3 ppbv
01:00	3.4	0
02:00	3.4	0
03:00	3.3	0
04:00	2.8	0
05:00	2.0	0
06:00	2.3	0
07:00	2.5	0
08:00	ND [a]	0
09:00	6.4	0
10:00	6.7	60
11:00	9.5	75
12:00	10.9	135
13:00	13.4	210
14:00	15.4	155
15:00	11.5	245
16:00	10.3	155
17:00	10.9	85
18:00	6.4	40
19:00	6.3	30
20:00	6.5	10
21:00		
22:00		
23:00		
24:00		

[a] ND = no data.

TABLE B-2-1.

Ambient Air Measurement of H_2O_2 July 24-29, 1979
Claremont, California.

	July 24	July 25	July 26	July 27	July 28	July 29
01:00	2.2	ND[a]	6.2	4.8	2.1	1.3
02:00	2.3	ND	ND	5.0	2.6	1.0
03:00	2.1	ND	ND	4.6	2.5	1.1
04:00	2.1	ND	ND	4.6	2.6	1.1
05:00	2.2	ND	ND	4.1	2.8	0.3
06:00	2.3	ND	ND	3.5	2.3	0.3
07:00	1.8	ND	ND	4.3	3.9	0.2
08:00	1.7	ND	ND	5.0	4.2	0.3
09:00	2.5	ND	ND	5.5	4.6	1.2
10:00	3.8	ND	ND	6.8	0.5	2.7
11:00	4.4	13.2	ND	6.2	2.4	3.4
12:00	4.8	13.1	6.2	5.7	3.6	3.5
13:00	6.0	12.4	11.6	6.7	4.5	4.4
14:00	5.7	11.5	11.2	8.5	4.2	4.4
15:00	5.6	8.5	11.0	11.5	5.2	3.5
16:00	ND	9.2	9.8	9.5	4.5	3.7
17:00	ND	8.8	8.4	5.9	4.2	4.2
18:00	ND	8.7	7.2	5.1	3.4	4.8
19:00	ND	9.5	5.3	4.2	3.2	4.8
20:00	ND	8.9	4.9	2.8	3.2	3.5
21:00	ND	8.2	4.2	2.7	3.6	3.6
22:00	ND	6.7	3.5	2.5	3.6	3.2
23:00	ND	6.2	3.3	2.6	1.8	2.6
24:00	ND	5.4	3.7	2.7	1.6	2.2

[a] ND = no data.

TABLE B-2-2. Ambient Air Measurements, July 24, 1979[a], Claremont, California.

Time PDT	Temp °C	RH %	O_3 ppbv	NO ppbv	NO_2 ppbv	Total S ppbv
01:00	22	74	0	20	70	21
02:00	21	78	0	20	60	21
03:00	19	85	0	20	80	21
04:00	19	90	0	20	80	19
05:00	17	90	0	30	80	19
06:00	18	86	0	20	80	18
07:00	18	88	0	20	60	18
08:00	18	80	0	60	80	23
09:00	19	60	10	80	100	31
10:00	21	80	ND[b]	40	90	35
11:00	26	42	130	20	80	35
12:00	28	38	220	10	70	31
13:00	31	34	290	10	80	26
14:00	32	32	340	0	50	25
15:00	33	31	360	0	60	30
16:00	33	32	ND	0	ND	ND
17:00	34	32	ND	0	60	26
18:00	34	34	ND	0	60	26
19:00	32	42	ND	0	60	28
20:00	31	50	110	0	60	26
21:00	28	62	80	0	60	25
22:00	25	72	30	0	60	22
23:00	23	78	10	0	70	22
24:00	22	82	10	0	70	22

[a] Data furnished by:

Dr. Bruce Appel
Air and Industrial Hygiene Laboratory
Berkeley, California

[b] ND = no data.

TABLE B-2-3. Ambient Air Measurements, July 25, 1979[a], Claremont, California.

Time PDT	Temp °C	RH %	O_3 ppbv	NO ppbv	NO_2 ppbv	Total S ppbv
01:00	21	84	10	10	60	60
02:00	20	84	10	10	70	70
03:00	20	88	10	20	60	60
04:00	20	90	10	40	50	50
05:00	19	92	10	40	50	50
06:00	17	100	0	50	50	50
07:00	23	88	0	40	50	50
08:00	27	64	10	40	60	60
09:00	30	50	60	20	70	70
10:00	32	40	110	0	50	50
11:00	33	35	160	0	60	60
12:00	35	32	210	10	40	40
13:00	34	30	240	0	40	40
14:00	33	28	250	0	30	30
15:00	32	26	250	0	40	40
16:00	30	28	210	0	40	40
17:00	28	30	180	0	60	60
18:00	24	32	150	0	60	60
19:00	22	44	100	0	80	80
20:00	21	58	90	0	80	80
21:00	19	66	30	0	90	90
22:00	18	72	10	0	90	90
23:00	18	78	0	0	90	90
24:00	17	84	0	20	80	80

[a] Data furnished by:

Dr. Bruce Appel
Air and Industrial Hygiene Laboratory
Berkeley, California

TABLE B-2-4. Ambient Air Measurements, July 26, 1979[a], Claremont, California.

Time PDT	Temp °C	RH %	O_3 ppbv	NO ppbv	NO_2 ppbv	Total S ppbv
01:00	15	74	10	0	30	18
02:00	15	68	10	0	30	19
03:00	14	70	10	0	30	22
04:00	14	74	10	0	20	ND[b]
05:00	14	74	0	0	30	23
06:00	14	60	ND	20	50	23
07:00	19	64	ND	60	60	25
08:00	22	52	ND	60	100	23
09:00	27	40	30	20	120	26
10:00	30	34	90	10	90	33
11:00	32	32	120	0	80	31
12:00	33	28	150	0	70	30
13:00	34	25	170	0	50	31
14:00	36	24	250	0	50	33
15:00	34	26	320	0	70	51
16:00	33	30	310	0	50	42
17:00	32	32	280	0	50	31
18:00	31	34	250	0	60	31
19:00	27	44	190	0	50	ND
20:00	24	50	80	0	70	ND
21:00	23	62	0	30	90	ND
22:00	21	68	ND	30	80	31
23:00	19	68	30	10	60	19
24:00	18	60	60	10	50	18

[a] Data furnished by:

Dr. Bruce Appel
Air and Industrial Hygiene Laboratory
Berkeley, California

[b] ND = no data.

TABLE B-2-5. Ambient Air Measurements, July 27, 1981[a], Claremont, California.

Time PDT	Temp °C	RH %	O_3 ppbv	NO ppbv	NO_2 ppbv	Total S ppbv
01:00	16	90	0	20	50	19
02:00	16	94	0	20	60	18
03:00	15	96	0	20	50	17
04:00	16	96	0	20	50	17
05:00	15	96	0	40	50	17
06:00	18	96	0	50	60	19
07:00	22	92	0	50	80	19
08:00	25	72	10	40	110	28
09:00	27	54	50	10	110	25
10:00	28	46	110	0	90	26
11:00	31	42	150	0	80	25
12:00	32	36	210	0	80	26
13:00	32	32	270	0	60	28
14:00	33	30	320	0	50	28
15:00	33	28	330	0	50	30
16:00	31	26	280	0	50	30
17:00	29	28	230	40	60	26
18:00	27	34	190	0	50	26
19:00	23	38	120	0	60	28
20:00	20	40	40	0	80	26
21:00	19	54	0	0	80	26
22:00	17	68	0	0	70	25
23:00	17	76	0	20	40	22
24:00	16	82	10	0	40	18

[a] Data furnished by:

Dr. Bruce Appel
Air and Industrial Hygiene Laboratory
Berkeley, California

TABLE B-2-6. Ambient Air Measurements, July 28, 1979[a], Claremont, California.

Time PDT	Temp °C	RH %	O_3 ppbv	NO ppbv	NO_2 ppbv	Total S ppbv
01:00	18	60	30	10	40	14
02:00	17	58	30	10	30	ND[b]
03:00	17	64	20	10	30	ND
04:00	17	65	20	10	30	ND
05:00	17	70	10	10	30	ND
06:00	17	50	10	10	30	21
07:00	17	60	20	10	50	21
08:00	20	50	50	10	70	18
09:00	23	38	110	10	70	21
10:00	28	32	140	10	70	30
11:00	32	31	200	10	70	19
12:00	33	28	240	10	60	19
13:00	34	25	280	10	50	19
14:00	36	25	270	10	50	ND
15:00	36	26	290	10	50	ND
16:00	36	28	290	10	50	ND
17:00	35	31	270	10	50	ND
18:00	33	32	210	10	50	ND
19:00	31	38	140	10	50	ND
20:00	29	50	110	10	50	ND
21:00	26	50	70	10	60	ND
22:00	23	60	40	10	60	ND
23:00	22	64	20	20	50	ND
24:00	20	64	10	10	50	ND

[a] Data furnished by:

Dr. Bruce Appel
Air and Industrial Hygiene Laboratory
Berkeley, California

[b] ND = no data.

TABLE: B-2-7. Ambient Air Measurements, July 29, 1979[a], Claremont, California.

Time PDT	Temp °C	RH %	O_3 ppbv	NO ppbv	NO_2 ppbv	Total S ppbv
01:00	20	60	60	10	30	ND[b]
02:00	19	60	60	10	30	ND
03:00	18	56	40	10	30	ND
04:00	18	60	60	10	30	ND
05:00	18	60	60	10	30	ND
06:00	17	64	30	10	30	19
07:00	17	62	20	10	60	42
08:00	17	62	80	10	70	40
09:00	21	58	110	10	60	35
10:00	23	48	160	10	50	26
11:00	29	40	210	10	40	26
12:00	31	36	240	10	30	19
13:00	33	34	280	10	40	22
14:00	36	28	290	10	50	26
15:00	37	26	240	10	50	31
16:00	37	26	200	10	50	31
17:00	36	28	270	10	50	40
18:00	35	30	260	10	50	38
19:00	33	32	220	10	50	33
20:00	31	38	120	10	60	33
21:00	29	48	80	10	70	31
22:00	26	64	30	10	70	28
23:00	23	76	20	10	50	25
24:00	21	85	30	10	50	25

[a] Data furnished by:

Dr. Bruce Appel
Air and Industrial Hygiene Laboratory
Berkeley, California

[b] ND = no data.

TABLE B-3-1: Ambient Air Measurements of HCHO, August 2-September, 1979 Claremont, California.

Date	Sampling Period Start	Finish	HCHO ppb
8-28-79	09:30	10:05	6.8
	10:25	10:55	6.7
	11:30	12:00	5.4
	12:47	13:17	5.6
	13:55	14:25	5.0
	15:25	15:15	10.0
8-29-79	10:45	11:15	8.8
	11:45	12:45	4.2
	13:35	14:15	9.7
	14:30	15:00	9.1
8-30-79	09:00	10:01	6.6
	10:01	11:02	7.8
	11:02	12:02	8.8
	12:02	13:00	9.0
	13:02	14:02	9.3
	14:05	15:00	9.2
8-31-79	12:00	12:30	9.4
	12:30	13:00	9.4
	13:01	13:31	11.0
	13:34	14:04	10.0
	14:04	14:29	8.9
	14:31	15:00	7.0
	15:02	15:30	4.9
	15:31	16:00	6.4
	16:02	16:30	7.2
	16:31	16:59	7.9
	17:01	17:30	8.1
9-1-79	06:57	07:56	12.0
	08:00	08:58	11.0
	09:00	09:58	7.2

TABLE B-3-2. Ambient Air Measurements of H_2O_2 (ppbv), August 27-September 2, 1979, Claremont, California.

Time	Aug. 27	Aug. 28	Aug. 29	Aug. 30	Aug. 31	Sept. 1	Sept. 2
01:00	0.9	0.6	0.3	1.6	0.9	0.6	ND[a]
02:00	0.9	0.6	0.3	1.4	0.9	0.8	ND
03:00	0.9	0.6	0.3	1.3	0.8	0.9	ND
04:00	0.8	0.6	0.6	0.9	0.9	0.8	ND
05:00	0.9	0.5	ND	0.6	0.6	1.1	ND
06:00	ND	0.3	0.6	0.6	0.3	0.9	ND
07:00	0.8	0.3	0.8	0.8	0.3	0.8	0.5
08:00	ND	0.2	0.5	1.1	0.6	0.8	0.8
09:00	0.1	0.2	0.6	1.3	0.8	0.8	1.1
10:00	0.5	0.6	0.8	1.6	0.8	1.4	1.1
11:00	0.9	0.6	0.6	1.4	0.9	0.9	1.6
12:00	1.2	0.8	ND	1.3	1.3	0.9	1.7
13:00	1.4	0.6	ND	1.4	1.6	1.3	2.2
14:00	ND	0.6	ND	1.9	1.6	1.4	2.2
15:00	ND	1.4	4.7	2.5	1.9	1.4	2.8
16:00	ND	2.8	5.5	2.5	1.7	1.9	1.7
17:00	ND	2.8	7.3	2.8	2.2	2.3	1.6
18:00	ND	2.2	6.6	2.2	1.7	1.9	1.3
19:00	0.9	1.3	3.3	2.2	1.9	1.1	1.3
20:00	0.9	1.1	2.8	1.9	1.7	0.8	1.1
21:00	0.8	0.8	2.5	1.9	1.3	0.8	1.3
22:00	0.8	0.6	2.5	1.9	1.3	0.8	1.3
23:00	0.6	0.6	1.9	1.6	0.8	0.5	ND
24:00	0.6	0.3	1.7		0.8	ND	ND

[a] ND = no data.

TABLE B-3-3. Ambient Air Measurements, August 27, 1979[a] Claremont, California.

Time PDT	CO ppmv	RH %	O_3 ppbv	NO ppbv	NO_2 ppbv	H_2O_2 ppbv
01:00	1.4	45	60	0	45	0.9
02:00	0.8	45	70	0	25	0.9
03:00	0.7	45	70	0	25	0.8
04:00	0.7	45	70	0	20	0.9
05:00	0.9	45	60	0	25	ND[b]
06:00	1.7	45	30	5	50	0.8
07:00	2.5	40	20	15	65	ND
08:00	3.3	40	10	30	80	0.1
09:00	5.5	50	20	45	125	0.5
10:00	4.0	45	70	10	100	0.9
11:00	2.6	45	125	5	65	1.2
12:00	3.2	45	145	5	100	1.4
13:00	2.9	40	190	0	80	ND
14:00	2.1	40	210	0	55	ND
15:00	1.8	35	205	0	55	ND
16:00	1.5	40	205	0	60	ND
17:00	1.3	40	195	0	60	ND
18:00	0.9	45	120	0	50	0.9
19:00	0.9	45	95	0	45	0.9
20:00	1.1	80	60	0	50	0.8
21:00	1.2	50	30	0	55	0.8
22:00	1.3	50	10	0	60	0.8
23:00	1.6	50	0	10	60	0.6
24:00	1.4	50	0	15	60	0.6

[a] Data taken from reference (32).

[b] ND = no data.

TABLE B-3-4. Ambient Air Measurements, August 28, 1979[a], Claremont, California.

Time PDT	CO ppmv	RH %	O_3 ppbv	NO ppbv	NO_2 ppbv	H_2O_2 ppbv
01:00	1.2	55	0	5	60	0.6
02:00	1.2	55	0	0	55	0.6
03:00	1.2	55	0	0	55	0.6
04:00	1.2	55	0	0	50	0.5
05:00	1.0	55	10	0	30	0.3
06:00	1.0	50	15	0	25	0.3
07:00	0.9	50	15	0	25	0.2
08:00	1.3	50	10	5	35	0.2
09:00	1.7	48	20	0	40	0.6
10:00	1.6	48	25	5	40	0.6
11:00	1.6	46	45	5	40	0.8
12:00	1.6	47	45	5	40	0.6
13:00	1.6	46	65	5	40	0.6
14:00	1.5	45	70	0	35	1.4
15:00	1.4	43	90	0	35	2.8
16:00	1.6	42	55	0	45	2.8
17:00	1.6	42	100	0	45	2.2
18:00	1.5	44	85	0	45	1.3
19:00	1.2	46	65	0	45	1.1
20:00	1.1	47	30	0	45	0.8
21:00	0.9	49	0	15	55	0.6
22:00	0.9	51	0	15	50	0.5
23:00	0.9	51	0	5	45	0.3
24:00	1.0	51	0	5	45	0.3

[a] Data taken from reference (32).

TABLE B-3-5. Ambient Air Measurements, August 29, 1979[a], Claremont, California.

Time PDT	CO ppmv	RH %	O_3 ppbv	NO ppbv	NO_2 ppbv	H_2O_2 ppbv
01:00	1.1	50	0	10	50	0.3
02:00	1.1	51	0	0	45	0.3
03:00	0.9	51	0	0	40	0.5
04:00	0.8	51	10	0	25	ND[b]
05:00	0.7	51	15	0	20	0.6
06:00	0.8	48	10	0	25	0.8
07:00	0.9	44	10	0	30	0.5
08:00	1.0	44	5	5	35	0.6
09:00	1.1	44	10	5	30	0.8
10:00	1.0	43	25	5	20	0.6
11:00	1.0	41	40	0	20	ND
12:00	1.3	40	50	5	25	ND
13:00	1.4	39	60	5	30	ND
14:00	1.1	39	75	0	25	4.7
15:00	1.1	42	75	0	25	5.5
16:00	1.1	43	70	5	35	7.3
17:00	1.3	44	75	5	40	6.6
18:00	1.5	45	75	0	45	3.3
19:00	1.5	47	60	0	50	2.8
20:00	1.6	50	25	0	65	2.5
21:00	1.5	52	15	0	55	2.5
22:00	1.3	54	10	0	50	1.9
23:00	1.2	52	10	0	45	1.7
24:00	1.4	53	0	5	55	1.6

[a] Data taken from reference (32).

[b] ND = no data.

TABLE B-3-6. Ambient Air Measurements, August 30, 1979[a] Claremont, California.

Time PDT	CO ppmv	RH %	O_3 ppbv	NO ppbv	NO_2 ppbv	H_2O_2 ppbv
01:00	1.4	42	0	5	55	1.4
02:00	1.5	49	0	20	55	1.3
03:00	1.5	49	0	30	50	0.9
04:00	1.3	51	0	25	50	0.6
05:00	1.3	52	0	25	50	0.6
06:00	1.5	50	0	35	45	0.8
07:00	2.1	46	0	72	45	1.1
08:00	1.9	45	0	45	45	1.3
09:00	1.6	45	10	20	55	1.6
10:00	1.1	42	20	15	40	1.4
11:00	0.6	36	45	5	25	1.3
12:00	0.5	34	60	5	25	1.4
13:00	0.5	34	75	0	25	1.9
14:00	0.7	34	105	0	30	2.5
15:00	0.7	33	125	0	35	2.5
16:00	0.7	31	145	0	40	2.8
17:00	0.8	39	155	0	40	2.2
18:00	0.9	42	105	0	45	2.2
19:00	1.1	45	75	0	50	2.2
20:00	1.6	49	65	0	50	1.9
21:00	1.8	51	35	0	50	1.9
22:00	1.9	51	10	0	50	1.9
23:00	2.1	53	0	10	65	1.6
24:00	2.5	52	0	30	60	0.9

[a] Data taken from reference (32).

TABLE B-3-7. Ambient Air Measurements, August 31, 1979[a], Claremont, California.

Time PDT	CO ppmv	RH %	O_3 ppbv	NO ppbv	NO_2 ppbv	H_2O_2 ppbv
01:00	2.3	51	5	15	55	0.9
02:00	2.4	51	5	15	50	0.8
03:00	2.2	51	5	5	45	0.9
04:00	2.1	50	10	5	40	0.6
05:00	2.3	50	10	5	40	0.3
06:00	2.6	49	5	15	45	0.3
07:00	3.5	46	0	50	50	0.6
08:00	3.7	46	5	45	55	0.8
09:00	2.5	49	30	5	40	0.8
10:00	2.7	45	40	10	60	0.9
11:00	2.5	43	75	5	60	1.3
12:00	2.0	38	105	0	45	1.6
13:00	1.7	34	135	0	35	1.6
14:00	1.6	30	155	0	35	1.9
15:00	1.5	26	180	0	40	1.7
16:00	1.5	24	180	0	40	2.2
17:00	1.5	24	135	0	50	1.7
18:00	1.6	26	140	0	50	1.9
19:00	1.8	28	100	0	60	1.7
20:00	2.1	29	50	0	70	1.3
21:00	2.3	34	10	0	75	0.9
22:00	2.3	35	0	5	75	0.8
23:00	2.4	36	0	15	70	0.8
24:00	2.6	39	0	25	70	0.6

[a] Data taken from reference (32).

TABLE B-3-8. Ambient Air Measurements, September 1, 1979[a], Claremont, California.

Time PDT	CO ppmv	RH %	O_3 ppbv	NO ppbv	NO_2 ppbv	H_2O_2 ppbv
01:00	3.0	42	0	40	70	0.8
02:00	3.2	44	0	35	70	0.9
03:00	3.2	45	0	40	70	0.8
04:00	3.0	45	0	25	65	1.1
05:00	2.8	45	0	15	65	0.9
06:00	2.7	46	5	0	65	0.8
07:00	2.6	45	5	5	55	0.8
08:00	2.7	45	10	5	60	0.8
09:00	2.9	45	15	10	70	1.4
10:00	3.1	42	30	15	65	0.9
11:00	3.1	40	50	10	55	0.9
12:00	2.9	37	80	5	50	1.3
13:00	2.4	36	105	0	35	1.4
14:00	1.9	34	160	0	30	1.4
15:00	1.9	32	180	0	30	1.9
16:00	1.7	30	160	0	30	2.3
17:00	1.5	29	200	0	40	1.9
18:00	1.7	30	230	0	50	1.1
19:00	2.1	31	180	0	55	0.8
20:00	2.2	34	80	0	60	0.8
21:00	2.3	38	30	0	70	0.6
22:00	2.5	41	0	10	85	0.5
23:00	2.8	42	5	15	75	ND[b]
24:00	2.8	44	15	10	70	ND

[a] Data taken from reference 32.

[b] ND = no data.

TABLE B-3-9. Ambient Air Measurements, September 2, 1979[a], Claremont, California.

Time PDT	CO ppmv	RH %	O_3 ppbv	NO ppbv	NO_2 ppbv	H_2O_2 ppbv
01:00	2.7	45	20	10	65	ND[b]
02:00	2.6	45	30	5	50	ND
03:00	2.3	44	40	0	40	ND
04:00	2.1	44	45	0	30	ND
05:00	2.0	42	40	0	30	ND
06:00	2.2	42	30	0	35	0.5
07:00	2.0	41	25	5	35	0.8
08:00	1.9	38	30	0	35	1.1
09:00	2.6	38	60	5	45	1.1
10:00	3.2	38	75	5	70	1.6
11:00	3.0	37	115	5	65	1.7
12:00	2.7	34	155	0	50	2.2
13:00	2.5	31	165	0	45	2.2
14:00	2.1	29	175	0	40	2.8
15:00	1.6	29	180	0	40	1.7
16:00	1.2	27	200	0	40	1.6
17:00	1.1	26	200	0	45	1.3
18:00	1.0	26	145	0	45	1.3
19:00	1.1	28	95	0	45	1.1
20:00	1.4	34	65	0	50	1.3
21:00	2.2	39	20	0	70	0.8
22:00	2.7	40	15	15	75	ND
23:00	3.4	40	20	20	90	ND
24:00	3.7	40	0	50	85	ND

[a] Data taken from reference 32.

[b] ND = no data.

TABLE B-4-1. Ambient Air Measurements, September 13-15. 1979, Claremont, California.

Sampling Period	H_2O_2 Period	Sampling Period	HCHO ppbv
September 13, 1979			
10:15-11:15	2.7	10:30-11:30	14
11:30-12:30	3.2	11:30-12:30	38
12:45-13:45	2.0	13:00-14:00	29
14:00-15:00	2.4	14:00-15:00	26
15:00-16:00	2.6		
20:30-21:30	1.6		
21:30-22:30	1.3		
22:30-23:30	1.3		
September 14, 1979			
23:30-00:30	1.1		
00:30-01:30	1.2		
01:30-02:30	0.9		
02:30-03:30	0.5		
03:30-04:30	1.3		
04:30-05:30	1.8		
05:30-06:30	2.2		
06:30-07:30	1.1		
07:30-08:30	0.9	07:15-08:15	8.5
08:30-09:30	1.0	08:30-09:30	13
09:30-10:30	1.8	10:00-11:00	12
		11:15-12:15	15
		12:45-13:45	16
14:30-15:30	1.8	14:00-15:00	21
15:30-16:30	1.5	15:15-16:14	17
16:30-17:30	1.3		
17:30-18:30	1.5		
18:30-19:30	1.0		
19:30-20:30	1.0		
20:30-21:30	0.8		
21:30-22:30	1.1		
22:30-23:30	1.2		
September 15, 1979			
23:30-00:30	1.1		
00:30-01:30	1.4		
01:30-02:30	1.8		
02:30-03:30	2.3		
03:30-04:30	1.6		
04:30-05:30	0.8		
05:30-06:30	1.1		

TABLE B-4-1, Continued

Sampling Period	H_2O_2 Period	Sampling Period	HCHO ppbv
06:30-07:30	1.3		
07:30-08:30	1.4		
08:30-09:30	1.3		
09:30-10:30	1.5		
10:30-11:30	2.3		
11:30-12:30	ND[a]	12:30-13:30	1.3
13:30-14:30	1.3		
14:30-15:30	1.4		
15:30-16:30	1.6		
16:30-17:30	1.5		
17:30-18:30	1.3		
18:30-19:30	1.3		
19:30-20:30	1.0		
20:30-21:30	0.9		
21:30-22:30	0.4		
22:30-23:30	0.4		

[a] ND = no data.

TABLE B-4-3. Ambient Air Measurements, September 13, 1979 Claremont, California.

Time PDT	O_3 ppbv	NO ppbv	NO_2 ppbv	PAN ppbv
01:00				
02:00				
03:00				
04:00				
05:00				
06:00				
07:00				
08:00				
09:00				
10:00				
11:00	100	0	180	11
12:00	160	0	140	9
13:00	230	0	130	10
14:00	290	0	100	9
15:00	280	0	90	9
16:00	340	0	90	10
17:00	380	0	100	14
18:00	280	0	110	12
19:00	190	0	120	10
20:00	100	0	110	7
21:00	40	0	120	4
22:00	10	0	130	4
23:00	10	0	120	3
24:00	10	10	110	2

TABLE B-4-3. Ambient Air Measurements, September 14, 1979, Claremont, California.

Time PDT	O_3 ppbv	NO ppbv	NO_2 ppbv	PAN ppbv
01:00	10	20	120	3
02:00	20	0	90	4
03:00	30	0	80	7
04:00	20	0	100	6
05:00	70	0	80	7
06:00	40	0	60	6
07:00	20	10	60	2
08:00	0	20	90	1
09:00	40	10	110	4
10:00	90	0	100	6
11:00	120	0	70	5
12:00	120	0	60	3
13:00	160	0	70	4
14:00	290	0	90	
15:00	330	0	80	10
16:00	280	0	70	11
17:00	250	0	70	6
18:00	150	0	80	4
19:00	70	0	80	2
20:00	30	0	90	1
21:00	0	40	110	1
22:00	0	70	120	1
23:00	10	15	90	2
24:00	20	0	80	4

TABLE B-4-4. Ambient Air Measurements, September 15, 1979, Claremont, California.

Time PDT	O_3 ppbv	NO ppbv	NO_2 ppbv
01:00	10	10	90
02:00	30	0	60
03:00	30	0	60
04:00	30	0	60
05:00	10	0	70
06:00	10	0	70
07:00	40	0	60
08:00	20	10	60
09:00	30	20	90
10:00	40	10	70
11:00	40	0	30
12:00	50	0	20
13:00	40	0	20
14:00	50	0	20
15:00	50	0	20
16:00	50	0	20
17:00	210	0	50
18:00	120	0	60
19:00	70	0	80
20:00	40	0	100
21:00	50	0	70
22:00	40	0	50
23:00	10	10	50
24:00	0	10	50

TABLE B-5-1 Ambient Air Measurement of HCHO, California State University -Los Angeles.

Date	Time (PDT)	HCHO (ppb) HMC-CL
	8:30-8:55	12
	9:08-9:58	10
	10:09-10:59	21
	11:14-12:04	23
	12:25-13:25	18
	13:53-14:43	21
	15:03-15:53	26
	16:12-17:02	31
	17:09-17:34	27
June 18, 1980	6:35-6:55	19
	7:32-8:02	22
	8:21-8:51	17
	9:12-9:42	34
	10:00-10:30	53
	10:49-11:19	36
	13:09-13:54	34
	14:03-14:48	28
	14:59-15:44	18
	15:58-16:43	20
	16:54-17:39	14
	17:56-18:42	37
	18:51-19:36	8
	19:45-20:30	ND
June 19, 1980	10:19-11:04	28
	11:10-12:05	33
	12:22-13:07	22
	13:18-13:53	26
	14:07-14:52	24
	15:04-15:49	23
	16:00-16:45	18
	17:08-17:53	12
June 20, 1980	7:00-7:45	9
	8:18-8:48	13
	9:05-9:35	16
	9:52-10:22	16
	10:37-11:07	18
	11:17-11:47	19
	11:58-12:28	18

TABLE B-5-2. Ambient Air Measurements, June 17, 1980
California State University-Los Angeles.

Time PDT	Temp. °C	RH %	NO ppbv	NO_2 ppbv	O_3 ppbv
01:00	13.0	95	ND	ND	20
02:00	13.0	100	115	84	20
03:00	13.0	95	66	66	24
04:00	12.5	95	60	65	27
05:00	12.5	95	50	54	28
06:00	13.0	95	44	45	31
07:00	13.0	90	46	50	30
08:00	15.5	85	55	50	28
09:00	17.5	70	50	52	30
10:00	21.0	65	45	55	41
11:00	23.5	65	44	60	46
12:00	25.0	60	45	60	50
13:00	26.0	55	45	59	63
14:00	26.5	55	41	60	81
15:00	26.5	55	40	62	97
16:00	26.0	60	40	62	97
17:00	24.5	65	41	61	107
18:00	22.0	75	40	58	75
19:00	21.0	85	39	62	52
20:00	18.5	90	38	62	44
21:00	15.5	95	37	68	37
22:00	13.5	95	36	56	33
23:00	13.0	100	38	56	28
24:00	13.5	95	36	58	30

TABLE B-5-3. Ambient Air Measurements, June 18, 1981
California State University-Los Angeles.

Time PDT	UV W/m^2	Temp. °C	RH %	H_2O_2 ppbv	NO ppbv	NO_2 ppbv	O_3 ppbv
01:00		13.5	90		36	59	27
02:00		13.0	90		36	56	32
03:00		12.5	95		36	54	30
04:00		12.5	95		34	55	29
05:00		12.5	90		35	53	31
06:00		13.0	90		34	54	30
07:00		13.0	80		40	50	24
08:00		13.5	75		35	51	29
09:00		16.0	60		38	51	30
10:00		17.5	60		42	56	32
11:00	31.2	21.0	55		46	66	48
12:00	36.2	26.5	55		42	68	71
13:00	37.2	28.5	55		39	72	114
14:00	36.5	29.5	50	2.6	37	67	135
15:00	33.4	29.5	50	2.5	34	64	118
16:00	26.9	27.0	55	1.0	37	58	136
17:00	19.8	26.5	60	1.0	37	58	90
18:00	10.0	22.0	75	0.9	40	55	72
19:00	4.0	22.0	75	0.8	36	53	52
20:00	0.9	20.5	80	0.8	35	63	38
21:00		16.0	85	0.6	32	65	32
22:00		14.5	85	0.6	28	66	25
23:00		13.5	90	0.4	40	68	21
24:00		13.5	90		63	68	25

TABLE B-5-4. Ambient Air Measurements, June 19, 1980, California State University-Los Angeles.

Time PDT	UV W/m^2	Temp. °C	RH %	H_2O_2 ppbv	NO ppbv	NO_2 ppbv	O_3 ppbv
01:00		13.0	90		54	69	21
02:00		13.0	90		63	63	22
03:00		12.5	95		51	64	21
04:00		12.5	90		66	69	26
05:00		12.5	90		70	70	27
06:00	0.7	12.5	85		88	67	25
07:00	4.9	14.5	70		55	53	24
08:00	10.8	18.5	70		133	75	27
09:00	16.9	20.0	65		123	102	33
10:00	23.5	24.0	60		72	120	43
11:00	29.4	26.5	60	2.4	67	125	60
12:00	34.0	27.0	55	2.0	40	125	95
13:00	36.2	28.0	55	2.1	29	115	111
14:00	30.6	30.5	45	1.7	28	94	194
15:00	29.7	30.5	45	2.1	20	90	162
16:00	18.6	27.5	55	1.9	17	89	117
17:00	11.1	24.0	60	2.2	18	85	86
18:00	4.0	22.5	60	2.2	18	73	68
19:00	0.4	20.5	75	2.1	20	74	34
20:00		17.0	80	2.5	22	94	24
21:00		15.5	80		60	100	25
22:00		14.0	85	1.5	56	80	23
23:00		14.0	90	1.3	127	66	24
24:00		14.0	90		121	60	24

TABLE B-5-5. Ambient Air Measurements, June 20, 1980, California State University-Los Angeles.

Time PDT	UV W/m^2	Temp. °C	RH %	H_2O_2 ppbv	NO ppbv	NO_2 ppbv	O_3 ppbv
01:00		13.5	90		121	60	24
02:00		13.0	90		82	60	25
03:00		13.0	90		76	58	24
04:00		13.5	90		80	54	23
05:00		13.5	90		84	53	25
06:00	1.0	14.5	85		104	55	24
07:00	4.7	16.0	65		182	61	27
08:00	10.8	18.5	65		175	72	30
09:00	17.6	22.0	55		97	95	34
10:00	24.1	24.5	50		63	97	42
11:00	30.8	26.0	50	0.9	38	101	72
12:00	36.6	28.5	45	1.3	27	96	99
13:00	38.2	31.0	45	1.4	19	76	145
14:00	37.0	32.0	40		18	65	147
15:00							
16:00							
17:00							
18:00							
19:00							
20:00							
21:00							
22:00							
23:00							
24:00							

TABLE B-5-6. HMC Hydrocarbon Analysis from CSLA

COLLECTED: 6/17/80 12:00-12:05		COLLECTED: 6/18/80 10:58-11:00	
ANALYZED: 6/18/80		Analyzed: 6/19/80	
$\mu g/m^3$	Hydrocarbon	$\mu g/m^3$	Hydrocarbon
16.0	Ethane	28.1	Ethane
7.3	Ethylene	7.1	Ethylene
11.8	Acetylene	16.0	Acetylene
16.5	Propane	34.5	Propane
2.7	Propene	5.1	Propene
6.2	Isobutane	10.0	Isobutane
13.3	n-Butane	37.4	n-Butane
1.0	1-Butene	2.7	1-Butene
--	Isobutene	--	Isobutene
--	2-Butene	--	2-Butene
13.5	Isopentane	18.3	Isopentane
12.7	n-Pentane	20.5	n-Pentane
--	1-Pentene	--	1-Pentene
--	2-Pentene	--	2-Pentene
	2-3 Dimethylbutane		2-3 Dimethylbutane
8.9	2-Methylpentane	11.2	2-Methylpentane
	3-Methylpentane		3-Methylpentane
	Methylcyclopentane		Methylcyclopentane
ND[a]	n-Hexane	ND	n-Hexane

[a] ND = no data.

TABLE B-5-7. HMC Hydrocarbon Analysis from CSLA

COLLECTED: 6/18/80 17:00-17:10		COLLECTED: 6/18/80 20:30-20:46	
ANALYZED: 6/19/80		Analyzed: 6/19/80	
$\mu g/m^3$	Hydrocarbon	$\mu g/m^3$	Hydrocarbon
25.4	Ethane	23.4	Ethane
13.7	Ethylene	5.7	Ethylene
19.1	Acetylene	9.7	Acetylene
20.8	Propane	20.4	Propane
4.3	Propene	3.5	Propene
6.7	Isobutane	7.1	Isobutane
15.8	n-Butane	14.1	n-Butane
1.5	1-Butene	--	1-Butene
1.4	Isobutene	1.1	Isobutene
1.7	2-Butene	1.0	2-Butene
25.5	Isopentane	13.2	Isopentane
23.6	n-Pentane	7.6	n-Pentane
--	1-Pentene	--	1-Pentene
--	2-Pentene	--	2-Pentene
	2-3 Dimethylbutane		2-3 Dimethylbutane
31.0	2-Methylpentane	9.3	2-Methylpentane
	3-Methylpentane		3-Methylpentane
	Methylcyclopentane		Methylcyclopentane
7.0	n-Hexane	2.9	n-Hexane

TABLE: B-6-1. Ambient Air Measurements, September 11-12, 1980, Palos Verdes, California.

Time PDT	HCHO ppbv	H_2O_2 ppbv	O_3 ppbv	Wind Direction
12:00		5.9	ND[a]	W
13:00		ND	ND	W
14:00		2.6	65	W
15:00	7.8	ND	65	W
16:00	ND	4.0	75	W
17:00	4.5	ND	60	W
18:00	ND	4.4	ND	W
19:00	3.2	ND	ND	NW
20:00	ND	3.4	80	NW
21:00	2.3	ND	80	NW
22:00	ND	1.9	95	N-NW
23:00	3.6	ND	90	N-NW
24:00	ND	1.9	ND	N-NW
01:00	5.5	ND	110	N-NW
02:00	ND	2.0	110	N-NW
03:00	19	ND	130	N-NW
04:00	ND	3.5	135	N-NW
05:00	31	5.5	120	SE
06:00	32	3.7	110	SE
07:00	22	4.2	120	S-SE
08:00	17	2.8	90	S-SE
09:00	17	3.1	130	S-SE
10:00	26	4.2	100	S-W
11:00	18	8.1	110	W
12:00	20	ND	ND	W

[a] ND = no data.

TABLE B-6-2.

HMC Hydrocarbon Analysis,
Claremont, California.

COLLECTED: 9/11/80 15:30-15:35		COLLECTED: 9/11/80 16:37-16:42	
ANALYZED: 9/19/80		ANALYZED: 9/15/80	
$\mu g/m^3$	Hydrocarbon	$\mu g/m^3$	Hydrocarbon
3.3	Ethane	0.8	Ethane
4.8	Ethylene	1.5	Ethylene
2.8	Acetylene	0.5	Acetylene
7.2	Propane	1.3	Propane
6.8	Propene	-	Propene
*	Isobutane	*	Isobutane
-	n-Butane	-	n-Butane
-	1-Butene	-	1-Butene
-	Isobutene	-	Isobutene
-	2-Butene	-	2-Butene
3.2	Isopentane	32.7	Isopentane
6.7	n-Pentane	32.1	n-Pentane
-	1-Pentene	-	1-Pentene
-	2-Pentene	-	2-Pentene
77	2-3 Dimethylbutane 2-Methylpentane 3-Methylpentane Methylcyclopentane	26.7	2-3 Dimethylbutane 2-Methylpentane 3-Methylpentane Methylcyclopentane
-	n-Hexane	16.1	n-Hexane
-	Unresolved C_6-C_7 including benzene	65.2	Unresolved C_6-C_7 including benzene
-	Toluene	-	Toluene

TABLE B-6-3.

HMC Hydrocarbon Analysis,
Claremont, California.

COLLECTED: 9/11/80 20:50-20:55		COLLECTED: 9/12/80 11:50-11:55	
ANALYZED: 9/20/80		ANALYZED: 9/16/80	
$\mu g/m^3$	Hydrocarbon	$\mu g/m^3$	Hydrocarbon
1.0	Ethane	1.4	Ethane
1.3	Ethylene	2.2	Ethylene
1.0	Acetylene	77.6	Acetylene
4.0	Propane	*	Propane
1.9	Propene	20.9	Propene
*	Isobutane	*	Isobutane
-	n-Butane	-	n-Butane
-	1-Butene	-	1-Butene
-	Isobutene	-	Isobutene
-	2-Butene	-	2-Butene
37.5	Isopentane	6.0	Isopentane
28.1	n-Pentane	40.1	n-Pentane
-	1-Pentene	-	1-Pentene
-	2-Pentene	-	2-Pentene
20.0	2-3 Dimethylbutane 2-Methylpentane 3-Methylpentane Methylcyclopentane	289	2-3 Dimethylbutane 2-Methylpentane 3-Methylpentane Methylcyclopentane
38.5	n-Hexane	40.9	n-Hexane
176	Unresolved C_6-C_7 including benzene	452	Unresolved C_6-C_7 including benzene
-	Toluene	146	Toluene

TABLE B-7-1.

Ambient Air Measurements,
Claremont, California.

Date	Sampling Time	HCHO (ppb) HMC-CL
9/19/80	0800-0845	NS [a]
	0900-0945	14.8
	1000-1045	4.7
	1100-1145	5.8
	1200-1245	4.6
	1300-1345	10.0
	1400-1445	6.0
	1500-1545	5.2
	1600-1645	4.1
	1700-1745	NS
9/25/80	0820-0840	18.7
	0900-0945	9.0
	1000-1045	9.6
	1100-1145	17.3
	1200-1245	11.9
	1400-1445	7.1
	1500-1545	NS
	1600-1645	22.6
	1700-1745	15.6
	1800-1845	12.4
	1900-2000	10.4
	2000-2100	8.5
	2100-2200	NS
	2200-2400	NS
9/26/80	0018-0200	1.6
	0200-0400	2.4
	0400-0600	2.4
	0600-0700	8.4
	0700-0800	5.9
	0800-0900	10.1
	0900-1000	7.4
	1000-1100	10.0
	1100-1200	11.7
	1200-1300	8.5
	1300-1400	9.6
	1400-1500	9.6
	1500-1600	8.2
	1600-1700	14.8
	1700-1800	10.1
	1800-1900	6.7
	1900-1945	6.8

TABLE B-7-1, continued

Date	Sampling Time	HCHO (ppb) HMC-CL
10/1/80	0910-1000	5.5
	1000-1100	0.3
	1200-1300	2.6
	1300-1400	13.2
	1400-1500	8.4
	1500-1600	5.9
	1600-1700	11.9
	1700-1800	16.7
	1800-1900	5.8
	1900-2000	4.7
10/2/80	0810-0900	6.1
	0900-1000	11.0
	1000-1100	11.7
	1100-1200	11.9
	1200-1300	8.6
	1325-1400	12.6
	1400-1500	9.8
	1500-1600	9.7
	1622-1700	14.3
	1700-1800	14.7
10/7/80		
	1217-1300	9.6
	1300-1345	10.6
	1400-1445	10.9
	1500-1545	12.3
10/8/80		
	1100-1145	21.5
	1200-1245	8.7
	1300-1345	13.2
	1400-1445	8.0

[a]NS = no sample.

TABLE B-7-2.

Formaldehyde Concentrations In The Particulate Phase, ppb
Claremont, California.

Date	Sampling Time	Volume Sampled m^3	HCHO HMC-CL	HCHO ERT-HPLC
9/25/80	0800-1200	5.08	0.140	- [a]
	1200-1600	5.08	0.184	0.118
	1600-2000	5.08	0.204	0.214
	2000-2400	5.08	0.212	-
9/26/80	0000-0400	5.08	0.160	0.142
	0400-0800	5.08	0.170	-
	0800-1200	5.08	0.280	0.146
	1200-1600	5.17	0.210	0.140
	1600-1940	5.17	0.188	0.066

[a] - = below detection limit

TABLE B-7-3. Ambient Air Measurements, September 25, 1980, Claremont, California.

TIME PDT	UV W/m^2	Temp. °C	RH %	H_2O_2 ppbv	O_3 ppbv
01:00		15.2			
02:00		14.8	46		
03:00		15.0			
04:00		14.3	46		
05:00		14.2			
06:00		13.8	36		
07:00	1.2	17.1			
08:00	4.2	18.0	31		
09:00	8.3	19.7			23
10:00	11.1	23.1	30		25
11:00	13.9	23.3			73
12:00	14.7	27.6	34	0.6	130
13:00	14.6	28.3		0.8	152
14:00	12.8	30.6	28	1.1	234
15:00	9.6	32.3		1.7	270
16:00	6.1	32.6	35	1.8	309
17:00	2.1	31.0		1.8	352
18:00	0.4	29.8	68	1.4	342
19:00		24.5		1.2	240
20:00		21.2	94	0.5	112
21:00		19.6		0.7	55
22:00		17.1	96	0.6	30
23:00		17.0		0.5	25
24:00		17.0		0.5	25

TABLE B-7-4. Ambient Air Measurements, September 26, 1980, Claremont, California.

Time PDT	UV W/m^2	Temp. °C	RH %	H_2O_2 ppbv	O_3 ppbv
01:00		15.8		0.8	29
02:00		16.0	80	0.7	35
03:00		16.0		0.8	55
04:00		14.2	85		83
05:00		14.4			60
06:00		14.5	60		52
07:00					42
08:00	1.1	16.0	70		30
09:00	3.7	21.1			35
10:00	8.0	23.8	68		45
11:00	11.2	26.9		0.6	57
12:00	13.8	28.2	53	0.8	85
13:00	14.2	29.1		1.2	135
14:00	14.9	31.5	39	1.0	157
15:00	12.7	31.8		1.4	158
16:00	9.2	31.4	44	1.4	210
17:00	5.5	30.2		1.1	255
18:00	2.6	26.9	69	1.7	325
19:00	0.5	22.0		1.1	313
20:00		19.1	95	0.6	182
21:00		17.3		0.2	73
22:00		15.9	98		31
23:00		14.4		0.2	20
24:00		14.1		0.5	20

TABLE B-7-5. Ambient Air Measurements, September 27, 1980, Claremont, California.

Time PDT	UV W/m^2	Temp. °C	RH %	O_3 ppbv
01:00		13.7		24
02:00		13.2	91	42
03:00		12.1		54
04:00		12.0	86	44
05:00		11.5		45
06:00		12.2	92	54
07:00		12.3		37
08:00	1.1	14.0	64	20
09:00	3.4	21.9		45
10:00	6.4	22.3	51	57
11:00	9.7	26.0		101
12:00	13.2	28.3	39	138
13:00	14.4	29.6	38	174
14:00	14.5	30.2	38	201
15:00	13.0	31.0		222
16:00	9.6	31.3	45	256
17:00	6.0	29.6		304
18:00	2.6	28.2	72	202
19:00	0.5	23.3		148
20:00		20.4	96	72
21:00		17.6		28
22:00		16.5	95	18
23:00		16.4		19
24:00		17.0	93	20

TABLE B-7-6. Ambient Air Measurements, September 28, 1980, Claremont, California.

Time PDT	UV W/m^2	Temp. °C	RH %	O_3 ppbv
01:00		16.2	93	31
02:00		15.9		31
03:00		16.4	91	32
04:00		15.5		56
05:00		16.0	81	21
06:00		17.1		34
07:00		17.0	75	44
08:00	1.1	17.9		42
09:00	3.9	22.0	43	46
10:00	8.0	29.8		68
11:00	11.4	33.1	35	110
12:00	13.9	35.4		126
13:00	14.8	36.2	35	136
14:00	13.4	37.0		168
15:00	13.2	38.1	30	192
16:00	9.9	34.2		194
17:00	6.2	35.8	33	201
18:00	2.6	25.0		235
19:00	0.4	30.1	72	172
20:00		26.5		102
21:00		22.9	96	59
22:00		20.0		37
23:00		19.3	63	37
24:00		19.0		52

TABLE B-7-8. Ambient Air Measurements, September 30, 1980, Claremont, California.

Time PDT	UV W/m^2	Temp. °C	RH %	O_3 ppbv
01:00		20.0	68	57
02:00		20.8		53
03:00		21.9	49	49
04:00		21.0		56
05:00		21.0	49	46
06:00		19.5		42
07:00		21.3	43	30
08:00	1.1	21.5		32
09:00	2.5	25.0	35	42
10:00	7.6	32.3		59
11:00	10.7	35.4	20	64
12:00	13.3	38.6		97
13:00	13.7	39.5	21	170
14:00	12.5	41.0		276
15:00	11.4	40.3	19	225
16:00	7.2	39.1		370
17:00	4.1	36.8	24	272
18:00	2.1	334		177
19:00	0.3	29.0	30	110
20:00		26.7		63
21:00		23.1	50	46
22:00		21.2		25
23:00		18.5	54	37
24:00		19.0		24

TABLE B-7-9. Ambient Air Measurements, October 1, 1980, Claremont, California.

Time PDT	UV W/m^2	Temp. °C	RH %	O_3 ppbv
01:00		18.0	52	33
02:00		18.0		40
03:00		17.2	40	41
04:00		17.1		40
05:00		16.5	41	34
06:00		16.7		22
07:00		17.0	42	18
08:00	1.0	18.1		21
09:00	3.8	22.9	34	26
10:00	7.4	28.5		49
11:00	10.7	31.0	19	54
12:00	12.8	33.2		85
13:00	13.5	33.6	15	90
14:00	12.1	34.1		160
15:00	10.5	36.0	16	262
16:00	7.8	36.6		270
17:00	4.0	34.2	38	375
18:00	1.8	31.9		278
19:00	0.3	27.3	61	215
20:00		22.8		165
21:00		21.0		90
22:00		19.6	84	45
23:00		18.3		23
24:00		19.0	93	66

TABLE B-7-10. Ambient Air Measurements, October 2, 1980, Claremont, California.

Time PDT	UV W/m^2	Temp. °C	RH %	O_3 ppbv
01:00		18.6	68	63
02:00		17.1		47
03:00		16.4	70	57
04:00		16.2		58
05:00		14.9	62	49
06:00		15.0		40
07:00		14.5	40	27
08:00	1.3	15.1		20
09:00	3.0	19.3	49	26
10:00	6.8	23.8		38
11:00	10.0	27.0	37	131
12:00	12.3	30.2		205
13:00	14.0	31.4	31	232
14:00	13.4	32.0		290
15:00	12.1	32.3	30	367
16:00	7.7	33.5		437
17:00	4.8	31.8	36	445
18:00	1.9	29.2		326
19:00	0.3	24.2	68	225
20:00		20.8		125
21:00		19.0	94	37
22:00		18.1		72
23:00		16.9	96	19
24:00		16.0		47

TABLE B-7-11. Ambient Air Measurements, October 6, 1980, Claremont, California.

Time PDT	UV W/m^2	Temp. °C	RH %	O_3 ppbv
01:00		17.1	76	
02:00		16.9		
03:00		17.3	85	
04:00		16.0		
05:00		15.8	92	
06:00		15.8		
07:00		16.2	64	
08:00	0.7	17.1		
09:00	3.0	21.5	60	
10:00	6.6	28.0		
11:00	8.2	31.3	54	
12:00	11.4	31.9		
13:00	12.9	34.1	49	
14:00	12.0	34.4		185
15:00	9.5	34.7	48	227
16:00	6.8	34.0		278
17:00	3.8	31.9	52	327
18:00	1.7	30.7		204
19:00	0.2	27.5	74	165
20:00		23.6		82
21:00		21.0	96	35
22:00		21.0		21
23:00		19.6	86	41
24:00		19.4		83

TABLE B-7-12. Ambient Air Measurements, October 7, 1980, Claremont, California.

TIME PDT	UV W/m^2	Temp. °C	RH %	O_3 ppbv
01:00		18.6	74	115
02:00		19.0		115
03:00		18.5	57	72
04:00		18.7		64
05:00		19.9	60	55
06:00		17.0		62
07:00		16.5	60	40
08:00	0.7	18.1		25
09:00	3.1	20.4	48	32
10:00	6.7	27.0		36
11:00	6.7	29.2	39	69
12:00	11.5	32.1		115
13:00	12.3	32.3	30	135
14:00	12.6	32.6		192
15:00	10.6	33.3	29	250
16:00	7.5	31.0		292
17:00	3.9	29.0	42	372
18:00	1.6	26.8		327
19:00	0.2	22.3	72	232
20:00		20.1		140
21:00		18.9	77	105
22:00		17.6		90
23:00		16.2	67	95
24:00		16.4		67

TABLE B-7-13. Ambient Air Measurements, October 8, 1980, Claremont, California.

Time PDT	UV W/m^2	Temp. °C	RH %	O_3 ppbv
01:00		16.4	43	108
02:00		14.0		60
03:00		14.1	46	67
04:00		14.1		55
05:00		13.8	45	47
06:00		14.0		37
07:00		13.5	53	19
08:00	0.7	13.2		20
09:00	1.6	26.7	50	45
10:00	6.7	28.1		64
11:00	8.9	31.0	35	78
12:00	10.9	23.6		142
13:00	12.9	26.2	36	190
14:00	12.4	27.5		255
15:00	10.7	28.0	42	303
16:00	8.0	27.9		
17:00	3.6	26.3	54	
18:00	0.8	24.2		
19:00				
20:00				
21:00				
22:00				
23:00				
24:00				

TABLE B-7-14. HMC Hydrocarbon Analysis, Claremont, California.

COLLECTED: 9/25/80 06:25-06:30		COLLECTED: 9/25/80 15:07-15:12	
ANALYZED: 9/30/80		Analyzed: 9/30/80	
$\mu g/m^3$	Hydrocarbon	$\mu g/m^3$	Hydrocarbon
13.1	Ethane	13.6	Ethane
12.4	Ethylene	2.9	Ethylene
20.1	Acetylene	20.3	Acetylene
6.1	Propane	5.4	Propane
2.4	Propene	0.8	Propene
7.9	Isobutane	5.5	Isobutane
14.8	n-Butane	10.4	n-Butane
--	1-Butene	--	1-Butene
--	Isobutene	--	Isobutene
--	2-Butene	--	2-Butene
19.1	Isopentane	10.5	Isopentane
12.2	n-Pentane	6.3	n-Pentane
--	1-Pentene	0.5	1-Pentene
--	2-Pentene	--	2-Pentene
	2-3 Dimethylbutane		2-3 Dimethylbutane
24.8	2-Methylpentane	80.6	2-Methylpentane
	3-Methylpentane		3-Methylpentane
	Methylcyclopentane		Methylcyclopentane
3.6	n-Hexane	3.7	n-Hexane

TABLE B-7-15.

HMC Hydrocarbon Analysis
Claremont, California.

COLLECTED: 9/25/80 17:15-17:20		COLLECTED: 9/25/80 21:30-21:35	
ANALYZED: 9/30/80		Analyzed: 9/30/80	
$\mu g/m^3$	Hydrocarbon	$\mu g/m^3$	Hydrocarbon
29.5	Ethane	15.3	Ethane
7.5	Ethylene	10.8	Ethylene
45.1	Acetylene	19.0	Acetylene
6.8	Propane	13.7	Propane
1.0	Propene	4.1	Propene
10.8	Isobutane	5.2	Isobutane
20.2	n-Butane	10.6	n-Butane
--	1-Butene	1.3	1-Butene
--	Isobutene	0.6	Isobutene
--	2-Butene	--	2-Butene
17.6	Isopentane	15.3	Isopentane
10.3	n-Pentane	8.6	n-Pentane
--	1-Pentene	0.5	1-Pentene
--	2-Pentene	1.0	2-Pentene
	2-3 Dimethylbutane		2-3 Dimethylbutane
12.3	2-Methylpentane	54.8	2-Methylpentane
	3-Methylpentane		3-Methylpentane
	Methylcyclopentane		Methylcyclopentane
3.7	n-Hexane	2.8	n-Hexane

TABLE B-8-1. Downtown Los Angeles HCHO Measurements[a], November 13, 1980.

Sample Time	HCHO ppbv
08:40-09:15	13.4
09:15-10:00	8.2
10:00-10:47	7.7
10:47-12:00	4.6
12:00-13:00	3.9
13:00-14:00	3.0
14:00-15:00	3.8
15:00-16:00	6.4
16:00-16:45	2.3

[a] Street-level sampling near the corner of Sixth and Hill Streets.